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(54) Abstract Title
Stabilizer mixture for organic materials

(57) Organic materials which possess outstanding stability to oxidative, thermal or light-induced degradation comprise as stabilizers at least one compound of the benzofuran-2-one type, at least one compound of the organic phosphite or phosphonite type, at least one compound of the phenolic antioxidant type and at least one compound of the sterically hindered amine type.

Stabilizer mixture for organic materials

The present invention relates to compositions comprising an organic material subject to oxidative, thermal or light-induced degradation, and as stabilizers at least one compound of the benzofuran-2-one type, at least one compound of the phosphite or phosphonite type, at least one compound of the phenolic antioxidant type and at least one compound of the sterically hindered amine type, and to the use thereof for stabilizing organic materials against oxidative, thermal or light-induced degradation.

The use of compounds of the benzofuran-2-one type as stabilizers for organic polymers is known, for example, from US 4,325,863; US 4,388,244; US 5,175,312; US 5,252,643; US 5,216,052; US 5,369,159; US 5,488,117; US 5,356,966; US 5,367,008; US 5,428,162; US 5,428,177 or US 5,516,920.

Organic phosphites, phosphonites and phosphoramides are known in the art as costabilizers, secondary antioxidants and processing stabilizers, inter alia for polyolefins. Examples of such known phosphite stabilizers can be found in R. Gächter/H. Müller (eds.), Plastics Additives Handbook, 3rd ed., page 47, Hanser, Munich 1990.

U.S. Patent 4,360,617 discloses that stabilizer mixtures comprising symmetrical triarylphosphites and certain phenolic antioxidants are particularly suitable for protecting certain organic materials, such as polyurethane, polyacrylonitrile, polyamide 12 or polystyrene, against oxidative, thermal or light-induced degradation.

Sterically hindered amines, including in particular compounds containing 2,2,6,6-tetramethylpiperidyl groups, are known as hindered amine light stabilizers (HALS).

The known stabilizers do not satisfy in every respect the high requirements which a stabilizer is required to meet, especially with regard to shelf life, water absorption, sensitivity to hydrolysis, in-process stabilization, colour properties, volatility, migration behaviour, compatibility and improvement in protection against light. As a result there continues to be a need for effective stabilizers for organic materials that are sensitive to oxidative, thermal and/or light-induced degradation.

It has now been found that a stabilizer mixture comprising at least one compound of the benzofuran-2-one type, at least one compound of the organic phosphite or phosphonite type, at least one compound of the phenolic antioxidant type and at least one compound of the sterically hindered amine type is particularly suitable as a stabilizer for organic materials which are sensitive to oxidative, thermal or light-induced degradation.

The present invention therefore provides compositions comprising

- a) an organic material which is subject to oxidative, thermal or light-induced degradation,
- b) at least one compound of the benzofuran-2-one type,
- c) at least one compound from the group of the organic phosphites or phosphonites,
- d) at least one compound from the group of the phenolic antioxidants, and
- e) at least one compound from the group of the sterically hindered amines.

Compositions which are of interest include those comprising as component (b) a compound of the formula I

in which, if n is 1,

R₁ is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-, C₁-C₄alkylamino-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl,

perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, or R_1 is a radical of the formula II

$$\begin{array}{c}
R_{9} \\
R_{7} \\
R_{8}
\end{array}$$

$$\begin{array}{c}
R_{10} \\
R_{11}
\end{array}$$
(II)

and

if n is 2,

 R_1 is unsubstituted or C_1 - C_4 alkyl- or hydroxyl-substituted phenylene or naphthylene; or is - R_{12} -X- R_{13} -,

 R_2 , R_3 , R_4 and R_5 independently of one another are hydrogen, chlorine, hydroxyl, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, C_1 - C_{25} alkanoyloxy, C_1 - C_{25} alkanoyloxy,

 C_3 - C_{25} alkanoyloxy which is interrupted by oxygen, sulfur or $N-R_{14}$; C_6 - C_9 cycloalkyl-

carbonyloxy, benzoyloxy or C_1 - C_{12} alkyl-substituted benzoyloxy; or else the radicals R_2 and R_3 or the radicals R_3 and R_4 or the radicals R_4 and R_5 , together with the carbon atoms to which they are attached, form a benzo ring, R_4 is additionally -(CH_2)_p- COR_{15} or -(CH_2)_qOH or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of the formula III

$$R_{2} \xrightarrow{O} H$$

$$R_{16} C - R_{17} \qquad (III)$$

in which R_1 is defined as indicated above for n=1, R_6 is hydrogen or a radical of the formula IV

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ R_3 & & & \\ & & & \\ R_4 & & \\ \end{array}$$
 (IV)

where R_4 is not a radical of the formula III and R_1 is defined as indicated above for n=1, R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, halogen, hydroxyl,

 C_1 - C_{25} alkyl, C_2 - C_{25} alkyl interrupted by oxygen, sulfur or $N-R_{14}$; C_1 - C_{25} alkoxy,

 C_2 - C_{25} alkoxy interrupted by oxygen, sulfur or $N-R_{14}$; C_1 - C_{25} alkylthio, C_3 - C_{25} alkenyl,

 C_3 - C_{25} alkenyloxy, C_3 - C_{25} alkynyl, C_3 - C_{25} alkynyloxy, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted or C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino,

C₁-C₂₅alkanoyl, C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or N-R₁₄;

 C_1 - C_{25} alkanoyloxy, C_3 - C_{25} alkanoyloxy interrupted by oxygen, sulfur or $N-R_{14}$;

C₁-C₂₅alkanoylamino, C₃-C₂₅alkenoyl, C₃-C₂₅alkenoyl interrupted by oxygen, sulfur or

substituted benzoyl; benzoyloxy or C1-C12alkyl-substituted benzoyloxy;

and R_8 or the radicals R_8 and R_{11} , together with the carbon atoms to which they are attached, form a benzo ring,

 R_{12} and R_{13} independently of one another are unsubstituted or C_1 - C_4 alkyl-substituted phenylene or naphthylene,

R₁₄ is hydrogen or C₁-C₈alkyl,

$$R_{15}$$
 is hydroxyl, $\left[-0^{-\frac{1}{r}}M^{r+}\right]$, C_{1} - C_{18} alkoxy or $-N$
 R_{25} ,

 R_{16} and R_{17} independently of one another are hydrogen, CF_3 , C_1 - C_{12} alkyl or phenyl, or R_{16} and R_{17} , together with the C atom to which they are attached, form a C_5 - C_8 cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C_1 - C_4 alkyl;

 R_{18} and R_{19} independently of one another are hydrogen, C_1 - C_4 alkyl or phenyl, R_{20} is hydrogen or C_1 - C_4 alkyl,

R₂₁ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl, C₂-C₂₅alkyl

interrupted by oxygen, sulfur or N-R₁₄; C₇-C₉phenylalkyl which is unsubstituted or

substituted on the phenyl radical from 1 to 3 times by C_1 - C_4 alkyl; C_7 - C_{25} phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C_1 - C_4 alkyl and

interrupted by oxygen, sulfur or $N-R_{14}$, or else the radicals R_{20} and R_{21} , together with

the carbon atoms to which they are attached, form a C₅-C₁₂cycloalkylene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

R₂₂ is hydrogen or C₁-C₄alkyl,

R₂₃ is hydrogen, C₁-C₂₅alkanoyl, C₃-C₂₅alkenoyl, C₃-C₂₅alkanoyl interrupted by oxygen, sulfur

or $N-R_{14}$; C_2-C_{25} alkanoyl substituted by a di(C_1-C_6 alkyl)phosphonate group;

C₆-C₉cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C₁-C₁₂alkyl-substituted benzoyl;

R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₈alkyl,

R₂₆ is hydrogen or C₁-C₈alkyl,

 R_{27} is a direct bond, C_1 - C_{18} alkylene, C_2 - C_{18} alkylene interrupted by oxygen, sulfur or

N-R₁₄; C₂-C₁₈alkenylene, C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene,

C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene, unsubstituted or C₁-C₄alkyl-substituted phenylene,

$$R_{28}$$
 is hydroxyl, $\left[-O^{-}\frac{1}{r}M^{r+}\right]$, C_1 - C_{18} -alkoxy or $-N$
 R_{25} ,

$$R_{29}$$
 is oxygen, -NH- or $N-C-NH-R_{30}$,

R₃₀ is C₁-C₁₈alkyl or phenyl,

R₃₁ is hydrogen or C₁-C₁₈alkyl,
M is an r-valent metal cation,
X is a direct bond, oxygen, sulfur or -NR₃₁-,
n is 1 or 2,
p is 0, 1 or 2,
q is 1, 2, 3, 4, 5 or 6,
r is 1, 2 or 3, and
s is 0, 1 or 2.

Unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-, C₁-C₄alkylamino-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, indolyl, indazolyl, purinyl, quinolizinyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl is, for example, 1-naphthyl, 2-naphthyl, 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl, 2-methoxy-1-naphthyl, 1-dimethylamino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-naphthyl, 1,2-1,3-dimethyl-6-naphthyl, dimethyl-7-naphthyl, 1,4-dimethyl-6-naphthyl, 1,5-dimethyl-2naphthyl, 1,6-dimethyl-2-naphthyl, 1-hydroxy-2-naphthyl, 2-hydroxy-1-naphthyl, 1,4-dihydroxy-2-naphthyl, 7-phenanthryl, 1-anthryl, 2-anthryl, 9-anthryl, 3-benzo[b]thienyl, 5-benzo-[b]thienyl, 2-benzo[b]thienyl, 4-dibenzofuryl, 4,7-dibenzofuryl, 4-methyl-7-dibenzofuryl, 2xanthenyl, 8-methyl-2-xanthenyl, 3-xanthenyl, 2-phenoxathiinyl, 2,7-phenoxathiinyl, 2-pyrrolyl, 3-pyrrolyl, 5-methyl-3-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 2-methyl-4-imidazolyl, 2-ethyl-4-imidazolyl, 2-ethyl-5-imidazolyl, 3-pyrazolyl, 1-methyl-3-pyrazolyl, 1-propyl-4-pyrazolyl, 2-pyrazinyl, 5,6-dimethyl-2-pyrazinyl, 2-indolizinyl, 2-methyl-3-isoindolyl, 2-methyl-1-isoindolyl, 1-methyl-2-indolyl, 1-methyl-3-indolyl, 1,5-dimethyl-2-indolyl, 1-methyl-3indazolyl, 2,7-dimethyl-8-purinyl, 2-methoxy-7-methyl-8-purinyl, 2-quinolizinyl, 3-isoquinolyl, 6-isoquinolyl, 7-isoquinolyl, isoquinolyl, 3-methoxy-6-isoquinolyl, 2-quinolyl, 6-quinolyl, 7-quinolyl, 2-methoxy-3-quinolyl, 2-methoxy-6-quinolyl, 6-phthalazinyl, 7-phthalazinyl, 1-methoxy-6-phthalazinyl, 1,4-dimethoxy-6-phthalazinyl, 1,8-naphthyridin-2-yl, 2-quinoxalinyl, 6-quinoxalinyl, 2,3-dimethyl-6-quinoxalinyl, 2,3-dimethoxy-6-quinoxalinyl, 2-quinazolinyl, 7-quinazolinyl,

2-dimethylamino-6-quinazolinyl, 3-cinnolinyl, 6-cinnolinyl, 7-cinnolinyl, 3-methoxy-7-cinnolinyl, 2-pteridinyl, 6-pteridinyl, 7-pteridinyl, 6,7-dimethoxy-2-pteridinyl, 2-carbazolyl, 3-carbazolyl, 9-methyl-2-carbazolyl, 9-methyl-3-carbazolyl, β-carbolin-3-yl, 1-methyl-β-carbolin-3-yl, 1-methyl-β-carbolin-6-yl, 3-phenanthridinyl, 2-acridinyl, 3-acridinyl, 2-perimidinyl, 1-methyl-5-perimidinyl, 5-phenanthrolinyl, 6-phenanthrolinyl, 1-phenazinyl, 2-phenazinyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 2-phenothiazinyl, 3-phenothiazinyl, 10-methyl-3-phenothiazinyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 4-methyl-3-furazanyl, 2-phenoxazinyl or 10-methyl-2-phenoxazinyl.

Particular preference is given to unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, isoindolyl, indolyl, phenothiazinyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, for example 1-naphthyl, 2-naphthyl, 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl, 2-methoxy-1-naphthyl, 1-dimethylamino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dimethyl-2-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dihydroxy-2-naphthyl, 1,6-dimethyl-2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 3-benzo[b]thienyl, 5-benzo[b]thienyl, 2-benzo[b]thienyl, 4-dibenzofuryl, 4,7-dibenzofuryl, 4-methyl-7-dibenzofuryl, 2-xanthenyl, 8-methyl-2-xanthenyl, 3-xanthenyl, 2-pyrrolyl, 3-pyrrolyl, 2-phenothiazinyl, 3-phenothiazinyl, 10-methyl-3-phenothiazinyl.

Halogen (halo) is, for example, chlorine, bromine or iodine. Preference is given to chlorine.

Alkanoyl having up to 25 carbon atoms is a branched or unbranched radical, for example formyl, acetyl, propionyl, butanoyl, pentanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, eicosanoyl or docosanoyl. Preference is given to alkanoyl having 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms. Particular preference is given to acetyl.

C₂-C₂₅alkanoyl substituted by a di(C₁-C₆alkyl)phosphonate group is, for example, (CH₃CH₂O)₂POCH₂CO-, (CH₃O)₂POCH₂CO-, (CH₃CH₂CH₂CH₂O)₂POCH₂CO-,

(CH₃CH₂O)₂POCH₂CH₂CO-, (CH₃O)₂POCH₂CH₂CO-, (CH₃CH₂CH₂CH₂CO)₂POCH₂CH₂CO-, (CH₃CH₂O)₂PO(CH₂)₄CO-, (CH₃CH₂O)₂PO(CH₂)₆CO- or (CH₃CH₂O)₂PO(CH₂)₁₇CO-.

Alkanoyloxy having up to 25 carbon atoms is a branched or unbranched radical, for example formyloxy, acetoxy, propionyloxy, butanoyloxy, pentanoyloxy, hexanoyloxy, heptanoyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, tridecanoyloxy, tetradecanoyloxy, pentadecanoyloxy, hexadecanoyloxy, heptadecanoyloxy, octadecanoyloxy, eicosanoyloxy or docosanoyloxy. Preference is given to alkanoyloxy having 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms. Particular preference is given to acetoxy.

Alkenoyl having 3 to 25 carbon atoms is a branched or unbranched radical, for example propencyl, 2-butencyl, 3-butencyl, isobutencyl, n-2,4-pentadiencyl, 3-methyl-2-butencyl, n-2-octencyl, n-2-dodecencyl, iso-dodecencyl, olecyl, n-2-octadecencyl or n-4-octadecencyl. Preference is given to alkencyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

 C_3 - C_{25} alkenoyl interrupted by oxygen, sulfur or $N-R_{14}$ is, for example,

CH3OCH2CH2CH=CHCO- or CH3OCH2CH2OCH=CHCO-.

Alkenoyloxy having 3 to 25 carbon atoms is a branched or unbranched radical, for example propenoyloxy, 2-butenoyloxy, 3-butenoyloxy, isobutenoyloxy, n-2,4-pentadienoyloxy, 3-methyl-2-butenoyloxy, n-2-octenoyloxy, n-2-dodecenoyloxy, iso-dodecenoyloxy, oleoyloxy, n-2-octadecenoyloxy or n-4-octadecenoyloxy. Preference is given to alkenoyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

C₃-C₂₅alkenoyloxy interrupted by oxygen, sulfur or N-R₁₄ is, for example,

CH₃OCH₂CH₂CH=CHCOO- or CH₃OCH₂CH₂OCH=CHCOO-.

C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or N-R₁₄ is, for example, CH₃-O-CH₂CO-,

CH₃-S-CH₂CO-, CH₃-NH-CH₂CO-, CH₃-N(CH₃)-CH₂CO-, CH₃-O-CH₂CH₂-O-CH₂CO-, CH₃-(O-CH₂CH₂-)₂O-CH₂CO-, CH₃-(O-CH₂CH₂-)₃O-CH₂CO- or CH₃-(O-CH₂CH₂-)₄O-CH₂CO-.

C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or N-R₁₄ is, for example,

CH₃-O-CH₂COO-, CH₃-S-CH₂COO-, CH₃-NH-CH₂COO-, CH₃-N(CH₃)-CH₂COO-, CH₃-O-CH₂CH₂-O-CH₂COO-, CH₃-(O-CH₂CH₂-)₂O-CH₂COO-, CH₃-(O-CH₂COO-, CH₃-(O-CH₂COO-)₄COO-.

 C_6 - C_9 cycloalkylcarbonyl is, for example, cyclohexylcarbonyl, cycloheptylcarbonyl or cyclooctylcarbonyl. Cyclohexylcarbonyl is preferred.

C₆-C₉cycloalkylcarbonyloxy is, for example, cyclohexylcarbonyloxy, cycloheptylcarbonyloxy or cyclooctylcarbonyloxy. Cyclohexylcarbonyloxy is preferred.

 C_1 - C_{12} alkyl-substituted benzoyl, which preferably carries 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylbenzoyl, 2,3-dimethylbenzoyl, 2,4-dimethylbenzoyl, 2,5-dimethylbenzoyl, 2,6-dimethylbenzoyl, 3,4-dimethylbenzoyl, 3,5-dimethylbenzoyl, 2-methyl-6-ethylbenzoyl, 4-tert-butylbenzoyl, 2-ethylbenzoyl, 2,4,6-trimethylbenzoyl, 2,6-dimethyl-4-tert-butylbenzoyl or 3,5-di-tert-butylbenzoyl. Preferred substituents are C_1 - C_8 alkyl, especially C_1 - C_4 alkyl.

 C_1 - C_{12} alkyl-substituted benzoyloxy, which preferably carries 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylbenzoyloxy, 2,3-dimethylbenzoyloxy, 2,4-dimethylbenzoyloxy, 2,5-dimethylbenzoyloxy, 2,6-dimethylbenzoyloxy, 3,4-dimethylbenzoyloxy, 3,5-dimethylbenzoyloxy, 2-methyl-6-ethylbenzoyloxy, 4-tert-butylbenzoyloxy, 2-ethyl-benzoyloxy, 2,4,6-trimethylbenzoyloxy, 2,6-dimethyl-4-tert-butylbenzoyloxy or 3,5-di-tert-butylbenzoyloxy. Preferred substituents are C_1 - C_8 alkyl, especially C_1 - C_4 alkyl.

Alkyl having up to 25 carbon atoms is a branched or unbranched radical, for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl,

isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl or docosyl. One of the preferred meanings of R_2 and R_4 is, for example, C_1 - C_{18} alkyl. A particularly preferred meaning of R_4 is C_1 - C_4 alkyl.

Alkenyl having 3 to 25 carbon atoms is a branched or unbranched radical, for example propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl. Preference is given to alkenyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

Alkenyloxy having 3 to 25 carbon atoms is a branched or unbranched radical, for example propenyloxy, 2-butenyloxy, 3-butenyloxy, isobutenyloxy, n-2,4-pentadienyloxy, 3-methyl-2-butenyloxy, n-2-octenyloxy, n-2-dodecenyloxy, iso-dodecenyloxy, oleyloxy, n-2-octadecenyloxy or n-4-octadecenyloxy. Preference is given to alkenyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

Alkynyl having 3 to 25 carbon atoms is a branched or unbranched radical, for example propynyl (—CH₂-C —CH), 2-butynyl, 3-butynyl, n-2-octynyl, or n-2-dodecynyl. Preference is given to alkynyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

Alkynyloxy having 3 to 25 carbon atoms is a branched or unbranched radical, for example propynyloxy (—OCH₂—C==CH), 2-butynyloxy, 3-butynyloxy, n-2-octynyloxy, or n-2-dodecynyloxy. Preference is given to alkynyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

 C_2 - C_{25} alkyl interrupted by oxygen, sulfur or $N-R_{14}$ is, for example, CH_3 -O- CH_2 -,

CH₃-S-CH₂-, CH₃-NH-CH₂-, CH₃-N(CH₃)-CH₂-, CH₃-O-CH₂CH₂-O-CH₂-, CH₃-(O-CH₂CH₂-)₂O-CH₂-, CH₃-(O-CH₂CH₂-)₃O-CH₂- or CH₃-(O-CH₂CH₂-)₄O-CH₂-.

 C_7 - C_9 phenylalkyl is, for example, benzyl, α -methylbenzyl, α , α -dimethylbenzyl or 2-phenylethyl. Benzyl and α , α -dimethylbenzyl are preferred.

 C_7 - C_9 phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C_1 - C_4 alkyl is, for example, benzyl, α -methylbenzyl, α , α -dimethylbenzyl, 2-phenylethyl, 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 2,4-dimethylbenzyl, 2,6-dimethylbenzyl or 4-tert-butylbenzyl. Benzyl is preferred.

 $C_T C_{25}$ phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C_1 - C_4 alkyl and is interrupted by oxygen, sulfur or $N - R_{14}$ is a branched or un-

branched radical, for example phenoxymethyl, 2-methylphenoxymethyl, 3-methylphenoxymethyl, 4-methylphenoxymethyl, 2,4-dimethylphenoxymethyl, 2,3-dimethylphenoxymethyl, phenylthiomethyl, N-methyl-N-phenylmethyl, N-ethyl-N-phenylmethyl, 4-tert-butylphenoxymethyl, 4-tert-butylphenoxymethyl, 2,4-di-tert-butylphenoxymethyl, 2,4-di-tert-butylphenoxymethyl, phenoxyethoxymethyl, benzyloxymethyl, benzyloxymethyl, N-benzyl-N-ethylmethyl or N-benzyl-N-isopropylmethyl.

 C_7 - C_9 phenylalkoxy is, for example, benzyloxy, α -methylbenzyloxy, α , α -dimethylbenzyloxy or 2-phenylethoxy. Benzyloxy is preferred.

C₁-C₄alkyl-substituted phenyl, which preferably contains 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methyl-6-ethylphenyl, 4-tert-butylphenyl, 2-ethylphenyl or 2,6-diethylphenyl.

C₁-C₄alkyl-substituted phenoxy, which preferably contains 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylphenoxy, 2,3-dimethylphenoxy, 2,4-dimethylphe-

noxy, 2,5-dimethylphenoxy, 2,6-dimethylphenoxy, 3,4-dimethylphenoxy, 3,5-dimethylphenoxy, 1,5-dimethylphenoxy, 2-ethylphenoxy, 2-ethylphenoxy, 2-diethylphenoxy, 2-ethylphenoxy, 2-diethylphenoxy, 2-diethylphenox

Unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl is, for example, cyclopentyl, methyl-cyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, trimethyl-cyclohexyl, tert-butylcyclohexyl, cycloheptyl or cyclooctyl. Preference is given to cyclohexyl and tert-butylcyclohexyl.

Unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy is, for example, cyclopentoxy, methylcyclopentoxy, dimethylcyclopentoxy, methylcyclohexoxy, dimethylcyclohexoxy, dimethylcyclohexoxy, trimethylcyclohexoxy, tert-butylcyclohexoxy, cycloheptoxy or cyclooctoxy. Preference is given to cyclohexoxy and tert-butylcyclohexoxy.

Alkoxy having up to 25 carbon atoms is a branched or unbranched radical, for example methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy, octoxy, decyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy. Preference is given to alkoxy having 1 to 12, especially 1 to 8, for example 1 to 6 carbon atoms.

C₂-C₂₅alkoxy interrupted by oxygen, sulfur or N-R₁₄ is, for example, CH₃-O-CH₂CH₂O-,

CH₃-S-CH₂CH₂O-, CH₃-NH-CH₂CH₂O-, CH₃-N(CH₃)-CH₂CH₂O-, CH₃-O-CH₂CH₂O-CH₂CH₂O-, CH₃-(O-CH₂CH₂-)₂O-CH₂CH₂O-, CH₃-(O-CH₂CH₂-)₃O-CH₂CH₂O- or CH₃-(O-CH₂CH₂-)₄O-CH₂CH₂O-.

Alkylthio having up to 25 carbon atoms is a branched or unbranched radical, for example methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, pentylthio, isopentylthio, hexylthio, heptylthio, octylthio, decylthio, tetradecylthio, hexadecylthio or octadecylthio. Preference is given to alkylthio having 1 to 12, especially 1 to 8, for example 1 to 6 carbon atoms.

Alkylamino having up to 4 carbon atoms is a branched or unbranched radical, for example methylamino, ethylamino, propylamino, isopropylamino, n-butylamino, isobutylamino or tert-butylamino.

Di(C₁-C₄alkyl)amino also means that the two radicals independently of one another are branched or unbranched, , for example dimethylamino, methylethylamino, diethylamino, methyl-n-propylamino, methylisopropylamino, methylisopropylamino, methylisopropylamino, methylisopropylamino, ethylisopropylamino, ethylisobutylamino, ethylisobutylamino, diethylamino, diisopropylamino, isopropyl-n-butylamino, isopropylisobutylamino, di-n-butylamino or diisobutylamino.

Alkanoylamino having up to 25 carbon atoms is a branched or unbranched radical, for example formylamino, acetylamino, propionylamino, butanoylamino, pentanoylamino, hexanoylamino, heptanoylamino, octanoylamino, nonanoylamino, decanoylamino, undecanoylamino, dodecanoylamino, tridecanoylamino, tetradecanoylamino, pentadecanoylamino, hexadecanoylamino, heptadecanoylamino, octadecanoylamino, eicosanoylamino or docosanoylamino. Preference is given to alkanoylamino having 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms.

C₁-C₁₈alkylene is a branched or unbranched radical, for example methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, dodecamethylene or octadecamethylene. Preference is given to C₁-C₁₂alkylene, especially C₁-C₈alkylene.

A C₁-C₄alkyl-substituted C₅-C₁₂cycloalkylene ring, which preferably contains 1 to 3, especially 1 or 2 branched or unbranched alkyl group radicals, is, for example, cyclopentylene, methylcyclopentylene, dimethylcyclopentylene, cyclohexylene, methylcyclohexylene, dimethylcyclohexylene, trimethylcyclohexylene, tert-butylcyclohexylene, cycloheptylene, cyclooctylene or cyclodecylene. Preference is given to cyclohexylene and tert-butylcyclohexylene.

 C_2 - C_{18} alkylene interrupted by oxygen, sulfur or $N-R_{14}$ is, for example, -CH₂-O-CH₂-,

-CH₂-S-CH₂-, -CH₂-NH-CH₂-, -CH₂-N(CH₃)-CH₂-, -CH₂-O-CH₂CH₂-O-CH₂-, -CH₂-(O-CH₂CH₂-)₃O-CH₂-, -CH₂-(O-CH₂CH₂-)₄O-CH₂- or -CH₂CH₂-S-CH₂CH₂-.

 C_2 - C_{18} alkenylene is, for example, vinylene, methylvinylene, octenylethylene or dodecenylethylene. Preference is given to C_2 - C_8 alkenylene.

Alkylidene having 2 to 20 carbon atoms is, for example, ethylidene, propylidene, butylidene, pentylidene, 4-methylpentylidene, heptylidene, nonylidene, tridecylidene, nonadecylidene, 1-methylethylidene, 1-ethylpropylidene or 1-ethylpentylidene. Preference is given to C_2 - C_8 al-kylidene.

Phenylalkylidene having 7 to 20 carbon atoms is, for example, benzylidene, 2-phenylethylidene or 1-phenyl-2-hexylidene. Preference is given to C_7 - C_9 -phenylalkylidene.

C₅-C₈cycloalkylene is a saturated hydrocarbon group having two free valencies and at least one ring unit and is, for example, cyclopentylene, cyclohexylene, cycloheptylene or cyclooctylene. Preference is given to cyclohexylene.

C₇-C₈bicycloalkylene is, for example, bicycloheptylene or bicyclooctylene.

Unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene is, for example, 1,2-, 1,3-, 1,4-phenylene, 1,2-, 1,3-, 1,4-, 1,6-, 1,7-, 2,6- or 2,7-naphthylene. 1,4-Phenylene is preferred.

A C₁-C₄alkyl-substituted C₅-C₈cycloalkylidene ring, which preferably contains 1 to 3, especially 1 or 2 branched or unbranched alkyl group radicals, is, for example, cyclopentylidene, methylcyclopentylidene, dimethylcyclopentylidene, cyclohexylidene, methylcyclohexylidene, dimethylcyclohexylidene, trimethylcyclohexylidene, tert-butylcyclohexylidene, cyclohexylidene or cyclooctylidene. Preference is given to cyclohexylidene and tert-butylcyclohexylidene.

A mono-, di- or trivalent metal cation is preferably an alkali metal, alkaline earth metal or aluminium cation, for example, Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺ or Al⁺⁺⁺.

Compositions that are of interest include those comprising as component (b) at least one compound of the formula I in which, if n is 1, R₁ is unsubstituted phenyl or phenyl which is substituted in the para position by C₁-C₁₈alkylthio or di(C₁-C₄alkyl)amino; mono- to penta-

substituted alkylphenyl having in total together not more than 18 carbon atoms in the 1 to 5 alkyl substituents; or is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl- or amino-substituted naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazolyl, thienyl, pyrrolyl, phenothiazinyl or 5,6,7,8-tetrahydronaphthyl.

Preference is given to compositions comprising as component (b) at least one compound of the formula I in which, if n is 2,

 R_1 is $-R_{12}$ -X- R_{13} -, R_{12} and R_{13} are phenylene, X is oxygen or -NR₃₁-, and R_{31} is C_1 - C_4 alkyl.

Preference is also given to compositions comprising as component (b) at least one compound of the formula I in which, if n is 1,

 R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, C_1 - C_4 alkylthio-, hydroxyl-, halo-, amino-, C_1 - C_4 alkylamino- or di(C_1 - C_4 -alkyl)amino-substituted naphthyl, phenanthryl, thienyl, dibenzofuryl, carbazolyl, fluorenyl or a radical of the formula II

$$\begin{array}{c} R_9 \\ R_{7} \\ R_{8} \end{array} \qquad \qquad \text{(II)}$$

R₇, R₈, R₉, R₁₀ and R₁₁ independently of one another are hydrogen, chlorine, bromine, hydroxyl, C₁-C₁₈alkyl, C₂-C₁₈alkyl interrupted by oxygen or sulfur; C₁-C₁₈alkoxy, C₂-C₁₈alkoxy interrupted by oxygen or sulfur; C₁-C₁₈alkylthio, C₃-C₁₂alkenyloxy, C₃-C₁₂alkynyloxy, C₇-C₉phenylalkyl, C₇-C₉phenylalkoxy, unsubstituted or C₁-C₄alkyl-substituted phenyl; phenoxy, cyclohexyl, C₅-C₈cycloalkoxy, C₁-C₄alkylamino, di(C₁-C₄-alkyl)amino, C₁-C₁₂alkanoyl, C₃-C₁₂alkanoyl interrupted by oxygen or sulfur; C₁-C₁₂alkanoyloxy, C₃-C₁₂alkanoyloxy interrupted by oxygen or sulfur; C₁-C₁₂alkanoylamino, C₃-C₁₂alkenoyl, C₃-C₁₂alkenoyloxy, cyclohexylcarbonyl, cyclohexylcarbonyloxy, benzoyl or C₁-C₄alkyl-substituted benzoyl; benzoyloxy or C₁-C₄alkyl-substituted benzoyloxy;

and R_8 or the radicals R_8 and R_{11} , together with the carbon atoms to which they are attached, form a benzo ring,

$$R_{15}$$
 is hydroxyl, C_1 - C_{12} alkoxy or N R_{25} ,

R₁8 and R₁9 independently of one another are hydrogen or C₁-C₄alkyl,

R₂₀ is hydrogen,

 R_{21} is hydrogen, phenyl, C_1 - C_{18} alkyl, C_2 - C_{18} alkyl interrupted by oxygen or sulfur; C_7 - C_9 phenylalkyl, C_7 - C_{18} -phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C_1 - C_4 alkyl and is interrupted by oxygen or sulfur, or else the radicals R_{20} and R_{21} , together with the carbon atoms to which they are attached, form a cyclohexylene ring which is unsubstituted or substituted from 1 to 3 times by C_1 - C_4 alkyl,

R₂₂ is hydrogen or C₁-C₄alkyl,

 R_{23} is hydrogen, C_1 - C_{18} alkanoyl, C_3 - C_{18} alkenoyl, C_3 - C_{12} alkanoyl interrupted by oxygen or sulfur; C_2 - C_{12} alkanoyl substituted by a di(C_1 - C_6 -alkyl)phosphonate group; C_6 - C_9 cycloalkyl-

carbonyl, benzoyl,
$$C_3H_{23}$$
 C_3H_{23} C_3H_{23} C_3H_{23} C_3H_{24} C_3H_{25} C_3H_{25}

R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₂alkyl,

R₂₆ is hydrogen or C₁-C₄alkyl,

 R_{27} is C_1 - C_{12} alkylene, C_2 - C_8 alkenylene, C_2 - C_8 alkylidene, C_7 - C_{12} phenylalkylidene, C_5 - C_8 Cycloalkylene or phenylene,

$$R_{28}$$
 is hydroxyl, C_1 - C_{12} alkoxy or N , R_{25} ,

R₂₉ is oxygen or -NH-, R₃₀ is C₁-C₁₈alkyl or phenyl, and s is 1 or 2.

Preference is likewise given to compositions comprising as component (b) at least one compound of the formula I in which, if n is 1,

 R_1 is phenanthryl, thienyl, dibenzofuryl, unsubstituted or C_1 - C_4 alkyl-substituted carbazolyl; or is fluorenyl; or R_1 is a radical of the formula II

$$\begin{array}{c} R_9 \\ R_7 \\ R_8 \end{array} \qquad \text{(II)}$$

R₇, R₈, R₉, R₁₀ and R₁₁ independently of one another are hydrogen, chlorine, hydroxyl, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₃-C₄alkenyloxy, C₃-C₄alkynyloxy, phenyl, benzoyl,

benzoyloxy or
$$-O-\overset{R_{20}}{\underset{-}{C}}\overset{R_{21}}{\underset{-}{C}}$$
 , H

R₂₀ is hydrogen,

 R_{21} is hydrogen, phenyl or C_1 - C_{18} alkyl, or else the radicals R_{20} and R_{21} , together with the carbon atoms to which they are attached, form a cyclohexylene ring which is unsubstituted or substituted from 1 to 3 times by C_1 - C_4 alkyl,

R₂₂ is hydrogen or C₁-C₄alkyl, and

R₂₃ is hydrogen, C₁-C₁₂alkanoyl or benzoyl.

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Particular preference is given to compositions comprising as component (b) at least one compound of the formula I in which, if n is 1,

 R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, C_1 - C_{12} alkyl, C_1 - C_4 alkylthio or phenyl.

Of particular interest are compositions comprising as component (b) at least one compound of the formula I in which

 R_2 , R_3 , R_4 and R_5 independently of one another are hydrogen, chlorine, C_1 - C_{18} alkyl, benzyl, phenyl, C_5 - C_8 cycloalkyl, C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_1 - C_{18} alkanoyloxy, C_1 - C_{18} alkenoyloxy or benzoyloxy; or else the radicals R_2 and R_3 or the radicals R_3 and R_4 or the radicals R_4 and R_5 , together with the carbon atoms to which they are attached, form a benzo ring, R_4 is additionally -(CH_2)_p- COR_{15} or -(CH_2)_qOH, or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of the formula III,

$$R_{15}$$
 is hydroxyl, C_1 - C_{12} alkoxy or N
 R_{25}

 R_{16} and R_{17} are methyl groups or, together with the C atom to which they are attached, form a C_5 - C_8 cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C_1 - C_4 alkyl,

 R_{24} and R_{25} independently of one another are hydrogen or C_1 - C_{12} alkyl, p is 1 or 2, and q is 2, 3, 4, 5 or 6.

Also of particular interest are compositions comprising as component (b) at least one compound of the formula I in which at least two of the radicals R_2 , R_3 , R_4 and R_5 are hydrogen.

Of special interest are compositions comprising as component (b) at least one compound of the formula I in which R_3 and R_5 are hydrogen.

Of very special interest are compositions comprising as component (b) at least one compound of the formula I in which

R₂ is C₁-C₄alkyl,

R₃ is hydrogen,

 R_4 is C_1 - C_4 alkyl or, if R_6 is hydrogen, R_4 is additionally a radical of the formula III,

R₅ is hydrogen, and

R₁₆ and R₁₇, together with the C atom to which they are attached, form a cyclohexylidene.

The following compounds are examples of the benzofuran-2-one type which are particularly suitable as component (b) in the novel composition: 3-[4-(2-acetoxyethoxy)phenyl]-5,7-ditert-butyl-benzofuran-2-one; 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one; 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one]; 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one; 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one; 5,7-di-tert-butyl-3-phenylbenzofuran-2-one; 5,7-di-tert-butyl-3-phenylbenzofuran-2-one; 5,7-di-tert-butyl-3-(2,3-dimethylphenyl)benzofuran-2-one.

Also of special interest are compositions comprising as component (b) at least one compound of the formula V

in which

R₂ is hydrogen or C₁-C₆alkyl,

R₃ is hydrogen,

R₄ is hydrogen or C₁-C₆alkyl,

R₅ is hydrogen,

 R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy, with the proviso that at least two of the radicals R_7 , R_8 , R_9 , R_{10} or R_{11} are hydrogen.

Very particular preference is given to compositions comprising as component (b) at least one compound of the formula Va or Vb

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or a mixture of the two compounds of the formula Va and Vb.

The compounds of the benzofuran-2-one type as component (b) in the novel composition are known in the literature and their preparation is described, for example, in the following US patents: US 4,325,863; US 4,388,244; US 5,175,312; US 5,252,643; US 5,216,052; US 5,369,159; US 5,488,117; US 5,356,966; US 5,367,008; US 5,428,162; US 5,428,177 or US 5,516,920.

Of particular interest are compositions comprising as component (c) at least one compound from the group of the organic phosphites or phosphonites of the formulae 1 to 7

(1)
$$R'_{1}-Y'-P$$

$$O-R'_{2}$$

$$O-R'_{3}$$

$$A'-X'-P$$

$$O-R'_{3}$$

$$D'-A'$$

$$R'_{3}-Q$$

$$A'$$

$$A'-X'-P$$

$$O-R'_{3}$$

$$A'-X'-P$$

$$O-R'_{3}$$

$$A'-X'-P$$

$$O-R'_{3}$$

$$A'-X'-P$$

$$O-R'_{3}$$

$$A'-X'-P$$

$$O-R'_{3}$$

$$O'-A'$$

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$$R'_{1}-O-P'_{0}-O'_{0}P-O-R'_{1}$$
 (5)

(6)
$$E' - P - Z' - R'_{14}$$
 R'_{15}
 R'_{15}
 R'_{14}
 R'_{14}
 R'_{14}
 R'_{14}
 R'_{14}
 R'_{14}

in which the indices are integral and

n' is 2, 3 or 4; p' is 1 or 2; q' is 2 or 3; r' is 4 to 12; y' is 1, 2 or 3; and z' is 1 to 6; A', if n' is 2, is C_2 - C_{18} alkylene; C_2 - C_{12} alkylene interrupted by oxygen, sulfur or -NR'₄-; a

radical of the formula
$$R_6'$$
 R_6'

A', if n' is 3, is a radical of the formula -C_rH_{2r-1}-;

A', if n' is 4, is
$$--CH_2$$
 $--CH_2$; $--CH_2$ $--CH_2$ $--CH_2$

A" has the meaning of A' if n' is 2;

B' is a direct bond, $-CH_{2}$ -, $-CHR'_{4}$ -, $-CR'_{1}R'_{4}$ -, sulfur or C_{5} - C_{7} cycloalkylidene, or is cyclohexylidene substituted by from 1 to 4 C_{1} - C_{4} alkyl radicals in position 3, 4 and/or 5; D', if p' is 1, is methyl and, if p' is 2, is $-CH_{2}$ OCH₂-;

E', if y' is 1, is C₁-C₁₈alkyl, -OR'₁ or halogen;

E', if y is 2, is -O-A*-O-,

E', if y is 3, is a radical of the formula R'₄C(CH₂O-)₃ or N(CH₂CH₂O-)₃;

Q' is the radical of an at least z'-valent alcohol or phenol, this radical being attached via the oxygen atom to the phosphorus atom;

 R'_{1} , R'_{2} and R'_{3} independently of one another are unsubstituted or halogen, -COOR₄', -CN- or -CONR₄'R₄'-substituted C₁-C₁₈alkyl; C₂-C₁₈alkyl interrupted by oxygen, sulfur or -NR'₄-; C₇-C₉phenylalkyl; C₅-C₁₂cycloalkyl, phenyl or naphthyl; naphthyl or phenyl substituted by halogen, 1 to 3 alkyl radicals or alkoxy radicals having in total 1 to 18 carbon atoms or by

integer from the range 3 to 6;

R'₄ is hydrogen, C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl or C₇-C₉phenylalkyl,

R'₅ and R'₆ independently of one another are hydrogen, C₁-C₈alkyl or C₅-C₆cycloalkyl,

R'₇ and R'₈, if q' is 2, independently of one another are C₁-C₄alkyl or together are a

2,3-dehydropentamethylene radical; and

R'₇ and R'₈, if q' is 3, are methyl;

R'14 is hydrogen, C1-C9alkyl or cyclohexyl,

R'₁₅ is hydrogen or methyl and, if two or more radicals R'₁₄ and R'₁₅ are present, these radicals are identical or different,

X' and Y' are each a direct bond or oxygen,

Z' is a direct bond, methylene, -C(R'16)2- or sulfur, and

R'16 is C1-C8alkyl.

Of particular interest are compositions comprising as component (c) a phosphite or phosphonite of the formula 1, 2, 5 or 6, in which

n' is the number 2 and y' is the number 1, 2 or 3;

A' is C₂-C₁₈alkylene, p-phenylene or p-biphenylene,

E', if y' is 1, is C₁-C₁₈alkyl, -OR'₁ or fluorine;

E', if y' is 2, is p-biphenylene,

E', if y' is 3, is N(CH₂CH₂O-)₃,

R'₁, R'₂ and R'₃ independently of one another are C_1 - C_{18} alkyl, C_7 - C_9 phenylalkyl, cyclohexyl, phenyl, or phenyl substituted by 1 to 3 alkyl radicals having in total 1 to 18 carbon atoms; R'₁₄ is hydrogen or C_1 - C_9 alkyl,

R'15 is hydrogen or methyl;

X' is a direct bond,

Y' is oxygen,

Z' is a direct bond or -CH(R'16)-, and

R'16 is C1-C4alkyl.

Likewise of interest are compositions comprising as component (c) a phosphite or phosphonite of the formula 1, 2, 5 or 6, in which

n' is the number 2 and y' is the number 1 or 3;

A' is p-biphenylene,

E', if y' is 1, is C₁-C₁₈alkoxy or fluorine,

E', if y' is 3, is $N(CH_2CH_2O_2)_3$,

 R'_1 , R'_2 and R'_3 independently of one another are C_1 - C_{18} alkyl, or are phenyl substituted by 2 or 3 alkyl radicals having in total 2 to 12 carbon atoms;

R'14 is methyl or tert-butyl;

R'15 is hydrogen;

X' is a direct bond;

Y' is oxygen; and

Z' is a direct bond, methylene or -CH(CH₃)-.

Particular preference is given to compositions comprising as component (c) a phosphite or phosphonite of the formula 1, 2 or 6.

Special preference is given to compositions comprising as component (c) at least one compound of the formula VII

$$\begin{bmatrix} R_2 & R_1 \\ R_3 & R_4 \end{bmatrix}_3$$
 (VIII)

in which

R₁ and R₂ independently of one another are hydrogen, C₁-C₈alkyl, cyclohexyl or phenyl, and

R₃ and R₄ independently of one another are hydrogen or C₁-C₄alkyl.

The following compounds are examples of organic phosphites and phosphonites which are particularly suitable as component (c) in the novel compositions.

Triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, triauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite (Irgafos® 168, Ciba-Geigy), diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite (formula D), bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite (formula E), bisisodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite (Irgafos®PEP-Q, Ciba-Geigy, formula H), 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocin (formula C), 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyldibenzo[d,g]-1,3,2-dioxaphosphocin (formula A), bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite (formula G).

Particular preference is given to the use of the following phosphites and phosphonites:

tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168, Ciba-Geigy), tris(nonylphenyl) phosphite,

$$(CH_3)_3C \longrightarrow C(CH_3)_3 \qquad (CH_3)_3C \longrightarrow C(CH_3)_3C \longrightarrow C(CH_3)_3 \qquad (CH_3)_3C \longrightarrow C(CH_3)_3C \longrightarrow C(CH_$$

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$$(CH_3)_3C$$
 $C(CH_3)_3$
 C
 $C(CH_3)_3$
 C
 $C(CH_3)_3$
 C
 $C(CH_3)_3$
 C
 $C(CH_3)_3$
 C
 $C(CH_3)_3$

$$(CH_3)_3C$$
 $C(CH_3)_3$ $C(CH_3)_4$ $C(CH$

$$H_3C$$
 $C(CH_3)_3$
 C
 $C(CH_$

(F)
$$H_{37}C_{18} = O - P_{O} = O - C_{18}H_{37}$$

$$H_{3}C = C - CH_{3} - C$$

$$\begin{bmatrix} C(CH_3)_3 \\ C(CH_3)_3 \end{bmatrix} = \begin{bmatrix} C(CH_3)_3 \\ C(CH_3)_3 \end{bmatrix}$$

$$(H)$$

Very particular preference is given to tris(2,4-di-tert-butylphenyl) phosphite [Irgafos°168, Ci-ba Spezialitätenchemie AG], bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite [Irgafos°38,

Ciba Spezialitätenchemie AG, formula (G)], or tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenyllenediphosphonite [Irgafos*PEP-Q, Ciba Spezialitätenchemie AG, formula (H)].

The abovementioned organic phosphites and phosphonites are known compounds; many of them are available commercially.

Compositions which are of interest include those comprising as component (d) at least one compound of the formula VI

$$\begin{bmatrix} H_3C & CH_3 \\ H_3C & CH_3 \\ HO & X & R_2 \end{bmatrix}$$
 (VI)

in which

R₁ is C₁-C₄alkyl,

n is 1, 2, 3 or 4,

if n is 1,

R₂ is C₁-C₂₅alkyl; and,

if n is 2,

 R_2 is C_2 - C_{12} alkylene, C_4 - C_{12} alkylene interrupted by oxygen or sulfur; or, if Y is -NH-, R_2 is additionally a direct bond; and,

if n is 3,

X is methylene or $-CH_2-C-O-CH_2-CH_2-$, where the ethylene group is attached to R₂, and

$$R_2$$
 is N N N ; and,

if n is 4.

R₂ is C₄-C₁₀alkanetetrayl.

Alkyl having up to 25 carbon atoms is a branched or unbranched radical, for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl or docosyl. A preferred definition of R_1 is methyl and tert-butyl. A particularly preferred definition of R_2 is C_1 - C_{20} alkyl, especially C_1 - C_{18} alkyl, for example C_4 - C_{18} alkyl. An especially preferred definition of R_2 is C_8 - C_{18} alkyl, especially C_{14} - C_{18} alkyl, for example C_{18} alkyl.

 C_2 - C_{12} alkylene is a branched or unbranched radical, for example ethylene, propylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene or dodecamethylene. A preferred definition of R_2 is, for example, C_2 - C_{10} alkylene, especially C_2 - C_8 alkylene. An especially preferred definition of R_2 is, for example, C_4 - C_8 alkylene, especially C_4 - C_6 alkylene, for example hexamethylene.

C₄-C₁₂alkylene interrupted by oxygen or sulfur can be interrupted one or more times and is, for example, -CH₂-O-CH₂-CH₂-O-CH₂-, -CH₂-(O-CH₂-CH₂-)₂O-CH₂-,

-CH₂-(O-CH₂CH₂-)₃O-CH₂-, -CH₂-(O-CH₂CH₂-)₄O-CH₂-,

-CH₂CH₂-O-CH₂CH₂-O-CH₂CH₂- or -CH₂CH₂-S-CH₂CH₂-. A preferred definition of R₂ is, for example, C₄-C₁₀alkylene interrupted by oxygen or sulfur, especially C₄-C₈alkylene interrupted by oxygen or sulfur, for example C₄-C₆alkylene interrupted by oxygen or sulfur. An especially preferred meaning of R₂ is -CH₂CH₂-O-CH₂CH₂-O-CH₂CH₂- or -CH₂CH₂-S-CH₂CH₂-.

Component (d) may also comprise mixtures of different sterically hindered phenols of the formula VI.

Compositions which are of interest include those comprising as component (d) at least one compound of the formula VI in which, if n is 1, R_2 is C_1 - C_{20} alkyl.

Preference is given to compositions comprising as component (d) at least one compound of the formula VI in which, if n is 2,

R₂ is C₂-C₈alkylene, C₄-C₈alkylene interrupted by oxygen or sulfur; or, if Y is -NH-, R₂ is additionally a direct bond; and,

if n is 4.

R₂ is C₄-C₈alkanetetrayl.

Preference is likewise given to compositions comprising as component (d) at least one compound of the formula VI in which

R₁ is methyl or tert-butyl,

n is 1, 2 or 4,

if n is 1,

R₂ is C₁₄-C₁₈alkyl; and,

if n is 2.

R₂ is C₄-C₆alkylene, or is C₄-C₆alkylene interrupted by oxygen; and

if n is 4,

R₂ is C₄-C₆alkanetetrayl.

Likewise of interest are compositions comprising as component (d) at least one compound of the formula VI in which the compound of the formula VI is a compound of the formula VIa to VIh

$$\begin{bmatrix}
H_3C & CH_3 \\
H_3C & CH_2 & CH_2 & C-NH & (CH_2)_3
\end{bmatrix}$$

$$H_3C & CH_3 & (VIa), Irganox on 1098$$

$$H_3C & CH_3 & CH_3$$

$$H_3C$$
 CH_3
 H_3C
 CH_2
 CH_2
 CH_2
 CH_2
 CH_3
 CH_3

$$\begin{bmatrix}
H_3C \\
H_3C
\end{bmatrix}$$

$$CH_2 - CH_2 - C - O - CH_2 - C$$

$$H_3C - CH_3$$

$$CH_3 - CH_2 - CH_2 - C - O - CH_2 - C$$

$$CH_3 - CH_3 - CH_3$$

- 32 -

$$R_3$$
 R_3 R_3 R_4 R_5 R_5 R_6 R_6 R_6 R_7 R_8 R_8 R_8 R_9 R_9

$$R_3$$
 R_3 R_3 R_4 R_5 R_5 R_6 R_6 R_7 R_8 R_8 R_8 R_8 R_9 R_9

Irganox°1098, irganox°1076, Irganox°1010, Irganox°245, Irganox°259, Irganox°3114, Irganox°1035 and Irganox°3125 are protected trade names of the company Ciba Spezialitätenchemie AG.

Preference is given to compositions comprising as component (d) at least one compound of the formula VI in which the compound of the formula VI is a compound of the formula VIa, VIb, VIc or VId, in particular a compound of the formula VIa, VIb or VIc.

Component (d) of the novel composition, and the compounds of the formula VI, are known and in some cases obtainable commercially. Possible preparation processes for the compounds of the formula VI can be found, for example, in the US Patents 3,330,859 or 3,960,928.

Compositions of interest include those comprising as component (e) at least one radical of the formula XII or XIII

(XII)
$$G = CH_{2} \xrightarrow{CH_{3}} G_{1}$$

$$G = CH_{2} \xrightarrow{CH_{3}} G_{2}$$

$$G = CH_{2} \xrightarrow{CH_{3}} G_{2}$$

$$G = CH_{2} \xrightarrow{CH_{3}} G_{1}$$

$$G = CH_{2} \xrightarrow{CH_{3}} G_{1}$$

$$G = CH_{2} \xrightarrow{CH_{3}} G_{2}$$

$$G = CH_{2} \xrightarrow{CH_{3}} G_{1}$$

in which

G is hydrogen or methyl, and

G₁ and G₂ are hydrogen, methyl or together are oxygen.

Of particular interest are compositions comprising as component (e) at least one compound from the group of the sterically hindered amines of the class of compounds described under (a') to (g'), which comprise at least one radical of the formula XII or XIII.

(a') Compounds of the formula XIIa

$$\begin{bmatrix}
G - CH_2 & G_1 \\
G_{11} & N & O \\
G - CH_2 & CH_3
\end{bmatrix}$$
(XIIa)

in which n is a number from 1 to 4,

G and G₁ independently of one another are hydrogen or methyl,

G₁₁ is hydrogen, O⁺, hydroxyl, NO, -CH₂CN, C₁-C₁₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl,

C₇-C₁₂aralkyl, C₁-C₁₈alkoxy, C₅-C₈cycloalkoxy, C₇-C₉phenylalkoxy, C₁-C₈alkanoyl,

C₃-C₅alkenoyl, C₁-C₁₈alkanoyloxy, benzyloxy, glycidyl or a group -CH₂CH(OH)-Z, where G₁₁ is preferably hydrogen, C₁-C₄alkyl, allyl, benzyl, acetyl or acryloyl,

Z is hydrogen, methyl or phenyl, and,

if n is 1,

G₁₂ is hydrogen, C₁-C₁₈alkyl, which is uninterrupted or interrupted by one or more oxygen atoms, or is cyanoethyl, benzyl, glycidyl, a monovalent radical of an aliphatic, cycloaliphatic, araliphatic, unsaturated or aromatic carboxylic acid, carbamic acid or phosphorus-containing acid or a monovalent silyl radical, preferably a radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, of an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms, it being possible for the carboxylic acid to be substituted in each case in the aliphatic, cycloaliphatic or aromatic moiety from 1 to 3 times by -COOZ₁₂, Z₁₂ is hydrogen, C₁-C₂₀alkyl, C₃-C₁₂alkenyl, C₅-C₇cycloalkyl, phenyl or benzyl, and, if n is 2,

G₁₂ is C₂-C₁₂alkylene, C₄-C₁₂alkenylene, xylylene, a divalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, dicarbamic acid or phosphorus-containing acid or a divalent silyl radical, preferably a radical of an aliphatic dicarboxylic acid having 2 to 36 carbon atoms, of a cycloaliphatic or aromatic dicarboxylic acid having 8 to 14 carbon atoms or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8 to 14 carbon atoms, it being possible for the dicarboxylic acid to be substituted in each case in the aliphatic, cycloaliphatic or aromatic moiety by 1 or 2 groups of -COOZ₁₂, and, if n is 3,

G₁₂ is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, which can be substituted in the aliphatic, cycloaliphatic or aromatic moiety by -COOZ₁₂, of an aromatic tricarbamic acid or of a phosphorus-containing acid, or is a trivalent silyl radical, and,

if n is 4,

G₁₂ is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

The carboxylic acid radicals indicated include in each case radicals of the formula (-CO)_nR, in which the meaning of n is indicated above and the meaning of R is evident from the definition stated.

Any C₁-C₁₂alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

As C_1 - C_{18} alkyl G_{11} or G_{12} can be, for example, the groups indicated above and also, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

If G₁₁ is C₃-C₈alkenyl it can, for example, be 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl or 4-tert-butyl-2-butenyl.

G₁₁ as C₃-C₈alkynyl is preferably propargyl.

G₁₁ as C₇-C₁₂aralkyl is especially phenethyl and in particular benzyl.

 G_1 : as C_1 - C_8 alkanoyl is, for example, formyl, propionyl, butyryl, octanoyl, but preferably acetyl and as C_3 - C_5 alkenoyl is especially acryloyl.

 G_{12} as a monovalent radical of a carboxylic acid is, for example, an acetic, caproic, stearic, acrylic, methacrylic, benzoic or β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid radical.

If G_{12} is a monovalent silyl radical then it is, for example, a radical of the formula $-(C_jH_{2j})-Si(Z')_2Z''$ in which j is an integer from the range from 2 to 5 and Z' and Z'' independently of one another are C_1-C_4 alkyl or C_1-C_4 alkoxy.

If G₁₂ is a divalent radical of a dicarboxylic acid then it is, for example, a malonic, succinic, glutaric, adipic, suberic, sebacic, maleic, itaconic, phthalic, dibutylmalonic, dibenzylmalonic, butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonic or bicycloheptenedicarboxylic acid radical.

If G₁₂ is a trivalent radical of a tricarboxylic acid then it is, for example, a trimellitic, citric or nitrilotriacetic acid radical.

If G_{12} is a tetravalent radical of a tetracarboxylic acid then it is, for example, the tetravalent radical of butane-1,2,3,4-tetracarboxylic acid or of pyromellitic acid.

If G₁₂ is a divalent radical of a dicarbamic acid then it is, for example, a hexamethylenedicarbamic or a 2,4-tolylenedicarbamic acid radical.

Preference is given to compounds of the formula XIIa in which G is hydrogen, G_{11} is hydrogen or methyl, n is 2 and G_{12} is the diacyl radical of an aliphatic dicarboxylic acid having 4 to 12 carbon atoms.

Examples of polyalkylpiperidine compounds of this class are the following compounds:

- 1) 4-Hydroxy-2,2,6,6-tetramethylpiperidine
- 2) 1-Allyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 3) 1-Benzyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 4) 1-(4-tert-Butyl-2-butenyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 5) 4-Stearoyloxy-2,2,6,6-tetramethylpiperidine
- 6) 1-Ethyl-4-salicyloyloxy-2,2,6,6-tetramethylpiperidine
- 7) 4-Methacryloyloxy-1,2,2,6,6-pentamethylpiperidine
- 8) 1,2,2,6,6-Pentamethylpiperidin-4-yl ß-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
- 9) Di(1-benzyl-2,2,6,6-tetramethylpiperidin-4-yl) maleate
- 10) Di(2,2,6,6-tetramethylpiperidin-4-yl) succinate
- 11) Di(2,2,6,6-tetramethylpiperidin-4-yl) glutarate
- 12) Di(2,2,6,6-tetramethylpiperidin-4-yl) adipate
- 13) Di(2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 14) Di(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate
- 15) Di(1,2,3,6-tetramethyl-2,6-diethylpiperidin-4-yl) sebacate

- 16) Di(1-allyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate
- 17) 1-Hydroxy-4-ß-cyanoethyloxy-2,2,6,6-tetramethylpiperidine
- 18) 1-Acetyl-2,2,6,6-tetramethylpiperidin-4-yl acetate
- 19) Tri(2,2,6,6-tetramethylpiperidin-4-yl) trimellitate
- 20) 1-Acryloyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine
- 21) Di(2,2,6,6-tetramethylpiperidin-4-yl) diethylmalonate
- 22) Di(1,2,2,6,6-pentamethylpiperidin-4-yl) dibutylmalonate
- 23) Di(1,2,2,6,6-pentamethylpiperidin-4-yl) butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonate
- 24) Di(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 25) Di(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 26) Hexane-1',6'-bis(4-carbamoyloxy-1-n-butyl-2,2,6,6-tetramethylpiperidine)
- 27) Toluene-2',4'-bis(4-carbamoyloxy-1-n-propyl-2,2,6,6-tetramethylpiperidine)
- 28) Dimethylbis(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 29) Phenyltris(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 30) Tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphite
- 31) Tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphate
- 32) Phenyl [bis(1,2,2,6,6-pentamethylpiperidin-4-yl)]phosphonate
- 33) 4-Hydroxy-1,2,2,6,6-pentamethylpiperidine
- 34) 4-Hydroxy-N-hydroxyethyl-2,2,6,6-tetramethylpiperidine
- 35) 4-Hydroxy-N-(2-hydroxypropyl)-2,2,6,6-tetramethylpiperidine
- 36) 1-Glycidyl-4-hydroxy-2,2,6,6-tetramethylpiperidine.
- (b') Compounds of the formula XIIb

$$\begin{bmatrix}
G - CH_2 & G_1 & G_{13} \\
G_{11} & N & N
\end{bmatrix}$$

$$G - CH_2 & CH_3 & G_{14}$$
(XIIb)

in which n is the number 1 or 2,

G, G₁ and G₁₁ are as defined under (a'),

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 G_{13} is hydrogen, C_1 - C_{12} alkyl, C_2 - C_5 hydroxyalkyl, C_5 - C_7 cycloalkyl, C_7 - C_8 aralkyl, C_2 - C_{18} alkanoyl, C_3 - C_5 alkenoyl, benzoyl or a group of the formula

and,

if n is 1,

G₁₄ is hydrogen, C₁-C₁₈alkyl, C₃-C₈alkenyl, C₅-C₇cycloalkyl, or C₁-C₄alkyl substituted by a hydroxyl, cyano, alkoxycarbonyl or carbamide group; glycidyl, a group of the formula -CH₂-CH(OH)-Z or of the formula -CONH-Z, in which Z is hydrogen, methyl or phenyl, and if n is 2,

 G_{14} is C_2 - C_{12} alkylene, C_6 - C_{12} arylene, xylylene, a - CH_2 -CH(OH)- CH_2 - group or a group - CH_2 -CH(OH)- CH_2 -O-D-O- in which D is C_2 - C_{10} alkylene, C_6 - C_{15} arylene, C_6 - C_{12} cycloalkylene, or, provided that G_{13} is not alkanoyl, alkenoyl or benzoyl, G_{14} can alternatively be 1-oxo- C_2 - C_{12} alkylene, a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or else can be the group -CO-, or,

if n is 1.

 G_{13} and G_{14} together can be the divalent radical of an aliphatic, cycloaliphatic or aromatic 1,2- or 1,3-dicarboxylic acid.

Any C₁-C₁₂- or C₁-C₁₈alkyl substituents are as already defined under (a').

Any C₅-C₇cycloalkyl substituents are, in particular, cyclohexyl.

 G_{13} as C_7 - C_8 aralkyl is in particular phenylethyl or especially benzyl. As C_2 - C_5 hydroxyalkyl G_{13} is, in particular, 2-hydroxyethyl or 2-hydroxypropyl.

G₁₃ as C₂-C₁₈alkanoyl is, for example, propionyl, butyryl, octanoyl, dodecanoyl, hexadecanoyl, octadecanoyl, but preferably acetyl, and as C₃-C₅alkenoyl is especially acryloyl.

If G₁₄ is C₂-C₈alkenyl it is, for example, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl or 2-octenyl.

G₁₄ as C₁-C₄alkyl substituted by a hydroxyl, cyano, alkoxycarbonyl or carbamide group can, for example, be 2-hydroxyethyl, 2-hydroxypropyl, 2-cyanoethyl, methoxycarbonylmethyl, 2-ethoxycarbonylethyl, 2-aminocarbonylpropyl or 2-(dimethylaminocarbonyl)ethyl.

Any C₂-C₁₂alkylene substituents are, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

Any C₆-C₁₅arylene substituents are, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

As C₆-C₁₂cycloalkylene particular mention may be made of cyclohexylene.

Preference is given to compounds of the formula lb in which n is 1 or 2, G is hydrogen, G_{11} is hydrogen or methyl, G_{13} is hydrogen, C_{1} - C_{12} alkyl or a group of the formula

and G_{14} , if n=1, is hydrogen or C_1 - C_{12} alkyl and, if n=2, is C_2 - C_8 alkylene or 1-oxo- C_2 - C_8 alkylene.

Examples of polyalkylpiperidine compounds of this class are the following compounds:

- 37) N,N'-Bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylene-1,6-diamine
- 38) N,N'-Bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylene-1,6-diacetamide
- 39) Bis(2,2,6,6-tetramethylpiperidin-4-yl)amine
- 40) 4-Benzoylamino-2,2,6,6-tetramethylpiperidine
- 41) N,N'-Bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dibutyladipamide

- 42) N,N'-Bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dicyclohexyl-2-hydroxypropylene-1,3-diamine
- 43) N,N'-Bis(2,2,6,6-tetramethylpiperidin-4-yl)-p-xylylenediamine
- 44) N,N'-Bis(2,2,6,6-tetramethylpiperidin-4-yl)succinamide
- 45) Di(2,2,6,6-tetramethylpiperidin-4-yl) N-(2,2,6,6-tetramethylpiperidin-4-yl)-ß-amino-dipropionate
- 46) The compound of the formula

$$\begin{bmatrix} CH_3 & CH_3$$

- 47) 4-(Bis-2-hydroxyethylamino)-1,2,2,6,6-pentamethylpiperidine
- 48) 4-(3-Methyl-4-hydroxy-5-tert-butylbenzamido)-2,2,6,6-tetramethylpiperidine
- 49) 4-Methacrylamido-1,2,2,6,6-pentamethylpiperidine
- (c') Compounds of the formula XIIc

$$\begin{bmatrix}
G - CH_2 & G_1 \\
G_{11} - N & O
\end{bmatrix}$$

$$G - CH_2 & CH_3$$

$$G - CH_3 & O$$

$$G - CH_2 & CH_3$$

$$G - CH_3 & O$$

$$G - CH_2 & CH_3$$

$$G - CH_3 & O$$

$$G - CH_3 &$$

in which n is the number 1 or 2, G, G_1 and G_{11} are as defined under (a'), and, if n is 1,

 G_{15} is C_2 - C_8 alkylene or C_2 - C_8 hydroxyalkylene or C_4 - C_{22} acyloxyalkylene, and, if n is 2,

 G_{15} is the group $(-CH_2)_2C(CH_2-)_2$.

If G_{15} is C_2 - C_8 alkylene or C_2 - C_8 hydroxyalkylene then it is, for example, ethylene, 1-methylethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

G₁₅ as C₄-C₂₂acyloxyalkylene is, for example, 2-ethyl-2-acetoxymethylpropylene.

Examples of polyalkylpiperidine compounds of this class are the following compounds:

- 50) 9-Aza-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 51) 9-Aza-8,8,10,10-tetramethyl-3-ethyl-1,5-dioxaspiro[5.5]undecane
- 52) 8-Aza-2,7,7,8,9,9-hexamethyl-1,4-dioxaspiro[4.5]decane
- 53) 9-Aza-3-hydroxymethyl-3-ethyl-8,8,9,10,10-pentamethyl-1,5-dioxaspiro[5.5]undecane
- 54) 9-Aza-3-ethyl-3-acetoxymethyl-9-acetyl-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 55) 2,2,6,6-Tetramethylpiperidine-4-spiro-2'-(1',3'-dioxane)-5'-spiro-5"-(1",3"-dioxane)-2"-spiro-4"'-(2"',2"',6"',6"'-tetramethylpiperidine).
- (d') Compounds of the formulae XIId, XIIe and XIIf, with compounds of the formula XIIf being preferred

$$\begin{bmatrix}
G - CH_2 & G_1 & G_{16} & O \\
G_{11} - N & C & O \\
G - CH_2 & CH_3 & O
\end{bmatrix}$$
(XIId)

$$G - CH_{2} \xrightarrow{CH_{3}} G_{1} \xrightarrow{G_{1}} O - C \xrightarrow{T_{1}} T_{2}$$

$$G - CH_{2} \xrightarrow{CH_{3}} H \xrightarrow{N - C} O$$
(XIIe)

$$G = CH_{2}$$

$$G = CH_{3}$$

$$G =$$

in which n is the number 1 or 2, G, G₁ and G₁₁ are as defined under (a'), G₁₆ is hydrogen, C₁-C₁₂alkyl, allyl, benzyl, glycidyl or C₂-C₆alkoxyalkyl, and, if n is 1,

 G_{17} is hydrogen, C_1 - C_{12} alkyl, C_3 - C_5 alkenyl, C_7 - C_9 aralkyl, C_5 - C_7 cycloalkyl, C_2 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_6 - C_{10} aryl, glycidyl or a group of the formula

-(CH₂)p-COO-Q or of the formula -(CH₂)p-O-CO-Q in which p is 1 or 2 and Q is C_1 - C_4 alkyl or phenyl, and,

if n is 2,

 G_{17} is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, C_6 - C_{12} arylene, a group -CH₂-CH(OH)-CH₂-O-D-O-CH₂-CH(OH)-CH₂- in which D is C_2 - C_{10} alkylene, C_6 - C_{15} arylene, C_6 - C_{12} cycloalkylene, or a group -CH₂CH(OZ')CH₂-(OCH₂-CH(OZ')CH₂)₂- in which Z' is hydrogen, C_1 - C_{18} alkyl, allyl, benzyl, C_2 - C_{12} alkanoyl or benzoyl,

 T_1 and T_2 independently of one another are hydrogen, C_1 - C_{18} alkyl or unsubstituted or haloor C_1 - C_4 alkyl-substituted C_6 - C_{10} aryl or C_7 - C_9 aralkyl or T_1 and T_2 , together with the carbon atom to which they are attached, form a C_5 - C_{14} cycloalkane ring.

Any C₁-C₁₂alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Any substituents in the meaning of C₁-C₁₈alkyl can, for example, be the groups listed above and also, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Any C₂-C₆alkoxyalkyl substituents are, for example, methoxymethyl, ethoxymethyl, propoxymethyl, tert-butoxymethyl, ethoxyethyl, ethoxypropyl, n-butoxyethyl, tert-butoxyethyl, isopropoxyethyl or propoxypropyl.

If G₁₇ is C₃-C₅alkenyl then it is, for example, 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

 G_{17} , T_1 and T_2 as C_7 - C_9 aralkyl are, in particular, phenethyl or especially benzyl. If T_1 and T_2 together with the carbon atom form a cycloalkane ring then this can, for example, be a cyclopentane, cyclohexane, cyclooctane or cyclododecane ring.

If G_{17} is C_2 - C_4 hydroxyalkyl then it is, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

 G_{17} , T_1 and T_2 as C_6 - C_{10} aryl are, in particular, phenyl, α - or β -naphthyl which are unsubstituted or substituted by halogen or C_1 - C_4 alkyl.

If G_{17} is C_2 - C_{12} alkylene then it is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

G₁₇ as C₄-C₁₂alkenylene is, in particular, 2-butenylene, 2-pentenylene or 3-hexenylene.

If G_{17} is C_6 - C_{12} arylene then it is, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

If Z' is C₂-C₁₂alkanoyl then it is, for example, propionyl, butyryl, octanoyl, dodecanoyl, but preferably acetyl.

D as C_2 - C_{10} alkylene, C_6 - C_{15} arylene or C_6 - C_{12} cycloalkylene is as defined under (b').

Examples of polyalkylpiperidine compounds of this class are the following compounds:

- 56) 3-Benzyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione
- 57) 3-n-Octyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione
- 58) 3-Allyl-1,3,8-triaza-1,7,7,9,9-pentamethylspiro[4.5]decane-2,4-dione
- 59) 3-Glycidyl-1,3,8-triaza-7,7,8,9,9-pentamethylspiro[4.5]decane-2,4-dione
- 60) 1,3,7,7,8,9,9-Heptamethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione
- 61) 2-Isopropyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane

- 62) 2,2-Dibutyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane
- 63) 2,2,4,4-Tetramethyl-7-oxa-3,20-diaza-21-oxodispiro[5.1.11.2]heneicosane
- 64) 2-Butyl-7,7,9,9-tetramethyl-1-oxa-4,8-diaza-3-oxospiro[4.5]decane and preferably:
- 65) 8-Acetyl-3-dodecyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

or the compounds of the following formulae:

66)
$$\begin{bmatrix} CH_3 & H & O \\ H_3C & N - C & OH \\ H_3C & CH_3 & O \end{bmatrix}$$

$$CH_3 & CH_2 - CH - CH_2 - O - CH_2 - CH - OH$$

67)
$$\begin{bmatrix} CH_{3} & H & O \\ H_{3}C & N - C \\ H_{3}C & N - CH_{2} - CH_{2} - CH_{2} \end{bmatrix}_{2}$$

$$\begin{bmatrix}
H_3C & H_3 & H_3C & H_3C$$

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(e') Compounds of the formula XIIg, which in turn are preferred

$$\begin{bmatrix}
G_{18} \\
N \\
G_{19}
\end{bmatrix}$$
(XIIg)

in which n is the number 1 or 2 and G₁₈ is a group of one of the formulae

$$G-CH_{2}$$

$$G_{11}$$

$$G-CH_{2}$$

$$G-CH_{2}$$

$$G-CH_{2}$$

$$G-CH_{2}$$

$$G-CH_{2}$$

$$G-CH_{3}$$

$$G-CH_{2}$$

$$G-CH_{3}$$

$$G-CH_{2}$$

$$G-CH_{3}$$

in which G and G11 are as defined under (a'),

 G_1 and G_2 are hydrogen, methyl or together are a substituent =0,

E is -O- or -NG₁₃-,

A is C2-C6alkylene or -(CH2)3-O-,

x is the number 0 or 1,

G₁₃ is hydrogen, C₁-C₁₂alkyl, C₂-C₅hydroxyalkyl or C₅-C₇cycloalkyl,

 G_{19} is the same as G_{18} or is one of the group -NG₂₁G₂₂, -OG₂₃, -NHCH₂OG₂₃ or -N(CH₂OG₂₃)₂,

 G_{20} , if n = 1, is the same as G_{18} or G_{19} and, if n = 2, G_{20} is a group -E-B-E-, in which B is C_2 - C_8 alkylene or C_2 - C_8 alkylene which is interrupted by 1 or 2 groups -N(G_{21})-,

G₂₁ is C₁-C₁₂alkyl, cyclohexyl, benzyl or C₁-C₄hydroxyalkyl or a group of the formula

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or a group of the formula

 G_{22} is C_1 - C_{12} alkyl, cyclohexyl, benzyl or C_1 - C_4 hydroxyalkyl, or G_{21} and G_{22} together are C_4 - C_5 alkylene or C_4 - C_5 oxaalkylene, for example - $CH_2CH_2OCH_2CH_2$ - or a group of the formula - $CH_2CH_2N(G_{11})CH_2CH_2$ -, and G_{23} is hydrogen, C_1 - C_{12} alkyl or phenyl.

Any C₁-C₁₂alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Any C₂-C₅hydroxyalkyl substituents are, for example, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxybutyl or 4-hydroxybutyl.

If A is C₂-C₆alkylene then it is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene.

If G₂₁ and G₂₂ together are C₄-C₅alkylene or oxaalkylene then this is, for example, tetramethylene, pentamethylene or 3-oxapentamethylene.

Examples of polyalkylpiperidine compounds of this class are the compounds of the following formulae:

71)
$$CH_3C$$
 CH_3
 CH

73)
$$\begin{array}{c}
CH_{3} \\
CH_{2} \\
CH_{2} \\
CH_{2}
\end{array}$$

$$\begin{array}{c}
CH_{3} \\
CH_{3} \\
CH_{3}
\end{array}$$

$$\begin{array}{c}
CH_{3} \\
CH_{3}
\end{array}$$

74)
$$\begin{array}{c} \text{RNHCH}_2\text{CH}_2 & \text{CH}_2\text{CH}_2\text{NHR} \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{H}_3\text{C} & \text{H}_3 & \text{H}_3\text{C} & \text{CH}_3 \\ \text{CH}_3 & \text{H}_3\text{C} & \text{CH}_3 & \text{CH}_3 \\ \end{array}$$

R has the same meaning as in compound 74.

76)
$$R' - NH - (CH2)3 - N - (CH2)2 - N - (CH2)3 - NH - R'$$

$$H_{3}C \xrightarrow{CH_{3}} N \xrightarrow{N} N \xrightarrow{N-C_{4}H_{9}} CH_{3}$$

$$H_{3}C \xrightarrow{CH_{3}} N \xrightarrow{N-C_{4}H_{9}} CH_{3}$$

R' has the same meaning as in compound 76.

80)
$$H_{3}C \longrightarrow CH_{2} \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow CH_{3} \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow CH_{3} \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow CH_{3} \longrightarrow CH_{3}$$

(f') Oligomeric or polymeric compounds whose structural repeating unit contains a 2,2,6,6-tetraalkylpiperidine radical, especially polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, poly(meth)acrylamides and copolymers thereof which include such radicals.

Examples of 2,2,6,6-polyalkylpiperidine compounds of this class are the compounds of the following formulae, in which m is a number from 2 to about 200.

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85)
$$\begin{array}{c|c}
 & OH \\
 & N-CH_2-CH-CH_2 \\
 & H_3C & CH_3 \\
 & H_3C & CH_3 \\
 & H_3C & H_3 \\
 &$$

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95)
$$\frac{\begin{bmatrix} R & R \\ I & I \\ N - (CH_2)_2 - N - (CH_2)_2 \end{bmatrix}_{m'}$$

in which R is a radical of the formula H = N H_3C CH_3 N = N

is a chain branch $-(CH_2)_2$, N, M' and M'' are each an integer from the range from M''

0 to 200, with the proviso that m' + m'' = m.

Further examples of polymeric compounds are reaction products of compounds of the formula

with epichlorohydrin; polyesters of butane-1,2,3,4-tetracarboxylic acid with a bifunctional alcohol of the formula

whose carboxyl side chains originating from the tetracarboxylic acid are esterified with 2,2,6,6-tetramethyl-4-hydroxypiperidine; compounds of the formula

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copolymers whose repeating unit is composed of two units

each case one unit
$$O = \begin{pmatrix} & & & \\ & &$$

(g') Compounds of the formula XIIIa

$$\begin{bmatrix}
G - CH_2 & CH_3 & O \\
G_{11} & N & N & G_{14}
\end{bmatrix}$$

$$G - CH_2 & CH_3 & O$$

$$G - CH_2 & CH_3 & O$$

$$G - CH_2 & O$$

$$G - CH_2 & O$$

$$G - CH_3 & O$$

$$G - CH_2 & O$$

$$G - CH_3 & O$$

$$G - CH_2 & O$$

$$G - CH_3 & O$$

$$G -$$

in which n is a number 1 or 2 and in which G and G11 are as defined under (a') and G14 is as defined under (b'), the meanings -CONH-Z and -CH2-CH(OH)-CH2-O-D-O- being excluded for G₁₄.

Examples of such compounds are:

100)
$$\begin{array}{c} H_3C \xrightarrow{CH_3} O \xrightarrow{CH_2} CH_2 \xrightarrow{CH_2} N \xrightarrow{CH_3} \\ H_3C \xrightarrow{CH_3} O \xrightarrow{CH_2-CH_2-N} N \xrightarrow{CH_3} \\ CH_3 \xrightarrow{CH_3} O \xrightarrow{CH_3-CH_2-N} O \xrightarrow{CH_3-CH_3-N} \\ \end{array}$$

101)
$$H_{3}C \longrightarrow N \longrightarrow N \longrightarrow CH_{2} \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow N \longrightarrow N \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow N \longrightarrow CH_{3}$$

$$H_{3}C \longrightarrow CH_{3} \longrightarrow N \longrightarrow CH_{2} \longrightarrow CH_{3} \longrightarrow CH_{3}$$

$$CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$$

H₃C
$$\stackrel{CH_3}{\longrightarrow}$$
 $\stackrel{O}{\longrightarrow}$ $\stackrel{O}{$

Of particular interest are compositions comprising as component (e) at least one compound of the formula H1, H2, H3, H4, H5, H6 and H7

$$H_{17}C_{8}O-N$$
 $H_{17}C_{8}O-N$
 $H_{3}C$
 CH_{3}
 CH_{3}
 $N-OC_{8}H_{17}$
 CH_{3}
 CH_{3}

(H2) Tinuvin^e144

$$H_3C$$
 CH_3
 CH_3

(H3) Tinuvin^e292

(H4) Tinuvin[®]622

(H5) Chimassorb 944

(H6) Chimassorb 119,

in which

m is a number from the range from 2 to 200.

Component (e) of the novel composition, or the compounds of the sterically hindered amine type, are known and some are commercially available.

Tinuvin^e123, Tinuvin^e144, Tinuvin^e292, Tinuvin^e622, Chimassorb^e944 und Chimassorb^e119 are protected trade names of Ciba Spezialitätenchemie AG.

As component (e) of the novel composition particular preference is given to the addition of those sterically hindered amines whose molecular weight or average molecular weight M_n is in the range from 500 to 10 000, in particular in the range from 1000 to 10 000. Of these, particular emphasis should again be placed on those sterically hindered amines whose molecular weight or average molecular weight M_n is in the range from 1500 to 10 000, for example in the range from 2000 to 7500.

Particular emphasis should be given to those novel compositions which as component (e) comprise two or more compounds of the sterically hindered amine type.

The mixture of components (b), (c), (d) und (e) is suitable for stabilizing organic materials against oxidative, thermal or light-induced degradation. Examples of such materials are:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

- a) radical polymerisation (normally under high pressure and at elevated temperature).
- b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, Vlb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either π- or σ-coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, Ila and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

- 2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).
- 3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.
- 4. Hydrocarbon resins (for example C₅-C₉) including hydrogenated modifications thereof (e.g. tackifiers) and mixtures of polyalkylenes and starch.
- 5. Polystyrene, poly(p-methylstyrene), poly(α -methylstyrene).
- 6. Copolymers of styrene or α -methylstyrene with dienes or acrylic derivatives, for example styrene/butadiene, styrene/acrylonitrile, styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate, styrene/butadiene/alkyl methacrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate; mixtures of high impact strength of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and block copolymers of styrene such as styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/ styrene.

- 7. Graft copolymers of styrene or α-methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene-styrene or polybutadiene-acrylonitrile copolymers; styrene and acrylonitrile (or methacrylonitrile) on polybutadiene; styrene, acrylonitrile and methyl methacrylate on polybutadiene; styrene and maleic anhydride on polybutadiene; styrene and maleimide on polybutadiene; styrene and maleimide on polybutadiene; styrene and alkyl acrylates or methacrylates on polybutadiene; styrene and acrylonitrile on ethylene/propylene/diene terpolymers; styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, as well as mixtures thereof with the copolymers listed under 6), for example the copolymer mixtures known as ABS, MBS, ASA or AES polymers.
- 8. Halogen-containing polymers such as polychloroprene, chlorinated rubbers, chlorinated and brominated copolymer of isobutylene-isoprene (halobutyl rubber), chlorinated or sulfo-chlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.
- 9. Polymers derived from α , β -unsaturated acids and derivatives thereof such as polyacrylates and polymethacrylates; polymethyl methacrylates, polyacrylamides and polyacrylonitriles, impact-modified with butyl acrylate.
- 10. Copolymers of the monomers mentioned under 9) with each other or with other unsaturated monomers, for example acrylonitrile/ butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/ alkyl methacrylate/butadiene terpolymers.
- 11. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine; as well as their copolymers with olefins mentioned in 1) above.

- 12. Homopolymers and copolymers of cyclic ethers such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
- 13. Polyacetals such as polyoxymethylene and those polyoxymethylenes which contain ethylene oxide as a comonomer; polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.
- 14. Polyphenylene oxides and sulfides, and mixtures of polyphenylene oxides with styrene polymers or polyamides.
- 15. Polyurethanes derived from hydroxyl-terminated polyethers, polyesters or polybutadienes on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.
- 16. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides starting from m-xylene diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4,-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, e.g. with polyethylene glycol, polypropylene glycol or polytetramethylene glycol; as well as polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing (RIM polyamide systems).
- 17. Polyureas, polyimides, polyamide-imides, polyetherimids, polyesterimids, polyhydantoins and polybenzimidazoles.
- 18. Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate and polyhydroxybenzoates, as well as block copolyether esters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.

- 19. Polycarbonates and polyester carbonates.
- 20. Polysulfones, polyether sulfones and polyether ketones.
- 21. Crosslinked polymers derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand, such as phenol/formaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins.
- 22. Drying and non-drying alkyd resins.
- 23. Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability.
- 24. Crosslinkable acrylic resins derived from substituted acrylates, for example epoxy acrylates, urethane acrylates or polyester acrylates.
- 25. Alkyd resins, polyester resins and acrylate resins crosslinked with melamine resins, urea resins, isocyanates, isocyanurates, polyisocyanates or epoxy resins.
- 26. Crosslinked epoxy resins derived from aliphatic, cycloaliphatic, heterocyclic or aromatic glycidyl compounds, e.g. products of diglycidyl ethers of bisphenol A and bisphenol F, which are crosslinked with customary hardeners such as anhydrides or amines, with or without accelerators.
- 27. Natural polymers such as cellulose, rubber, gelatin and chemically modified homologous derivatives thereof, for example cellulose acetates, cellulose propionates and ceilulose butyrates, or the cellulose ethers such as methyl cellulose; as well as rosins and their derivatives.
- 28. Blends of the aforementioned polymers (polyblends), for example PP/EPDM, Polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR,

POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PBT/PC/ABS or PBT/PET/PC.

29. Naturally occurring and synthetic organic materials which are pure monomeric compounds or mixtures of such compounds, for example mineral oils, animal and vegetable fats, oil and waxes, or oils, fats and waxes based on synthetic esters (e.g. phthalates, adipates, phosphates or trimellitates) and also mixtures of synthetic esters with mineral oils in any weight ratios, typically those used as spinning compositions, as well as aqueous emulsions of such materials.

30. Aqueous emulsions of natural or synthetic rubber, e.g. natural latex or latices of carboxylated styrene/butadiene copolymers.

The mixture of components (b), (c), (d) and (e) is likewise used for polyurethane production, especially for preparing flexible polyurethane foams. In this context the novel compositions and the products produced therefrom are effectively protected against degradation. In particular, scorching during foam production is avoided.

The polyurethanes are obtained, for example, by reacting polyethers, polyesters and polybutadienes which contain terminal hydroxyl groups with aliphatic or aromatic polyisocyanates.

Polyethers having terminal hydroxyl groups are known and are prepared, for example, by polymerizing epoxides such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin with themselves, for example in the presence of BF₃, or by addition reaction of these epoxides, alone or as a mixture or in succession, with starting components containing reactive hydrogen atoms, such as water, alcohols, ammonia or amines, for example ethylene glycol, propylene 1,3- and 1,2-glycol, trimethylolpropane, 4,4'-dihydroxydiphenylpropane, aniline, ethanolamine or ethylenediamine. Sucrose polyethers are also suitable in accordance with the invention. In many cases preference is given to those polyethers which predominantly (up to 90% by weight, based on all the OH groups present in the polyether) contain primary OH groups. Furthermore, polyethers modified by vinyl polymers, as are formed, for example, by polymerizing styrene and acrylonitrile in the presence of polyethers, are suitable, as are polybutadienes containing OH groups.

These compounds generally have molecular weights of 400-10000 and are polyhydroxy compounds, especially compounds containing from two to eight hydroxyl groups, especially those of molecular weight from 800 to 10 000, preferably from 1000 to 6000, for example polyethers containing at least 2, generally 2 to 8, but preferably 2 to 4, hydroxyl groups, as are known per se for the preparation of homogeneous polyurethanes and cellular polyurethanes.

It is of course possible to employ mixtures of the above compounds containing at least two isocyanate-reactive hydrogen atoms, in particular with a molecular weight of 400 - 10 000.

Suitable polyisocyanates are aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates, for example ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane 1,3-diisocyanate, cyclohexane 1,3- and -1,4-diisocyanate and also any desired mixtures of these isomers, 1isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 2,4- and 2,6-hexahydrotolylene diisocyanate and also any desired mixtures of these isomers, hexahydro-1,3- and/or -1,4phenylene diisocyanate, perhydro-2,4'- and/or -4,4'-diphenylmethanediisocyanate, 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate, and also any desired mixtures of these isomers, diphenylmethane 2,4'- and/or -4,4'-diisocyanate, naphthylene 1,5diisocyanate, triphenylmethane 4,4',4"-triisocyanate, polyphenyl-polymethylene polyisocyanates as are obtained by aniline-formaldehyde condensation followed by phosgenization, mand p-isocyanatophenylsulfonyl isocyanates, perchlorinated anyl polyisocyanates, polyisocyanates containing carbodiimide groups, polyisocyanates containing allophanate groups, polyisocyanates containing isocyanurate groups, polyisocyanates containing urethane groups, polyisocyanates containing acylated urea groups, polyisocyanates containing biuret groups, polyisocyanates containing ester groups, reaction products of the abovementioned isocyanates with acetals, and polyisocyanates containing polymeric fatty acid radicals.

It is also possible to employ the isocyanate group-containing distillation residues, as they are or dissolved in one or more of the abovementioned polyisocyanates, which are obtained in the course of the industrial preparation of isocyanates. It is additionally possible to use any desired mixtures of the abovementioned polyisocyanates.

Particular preference is given in general to the polyisocyanates which are readily obtainable industrially, for example 2,4- and 2,6-tolylene diisocyanate and any desired mixtures of these isomers ("TDI"), polyphenyl-polymethylene-polyisocyanates as prepared by aniline-formal-dehyde condensation followed by phosgenization ("crude MDI"), and polyisocyanates containing carbodiimide, urethane, allophanate, isocyanurate, urea or biuret groups ("modified polyisocyanates").

The organic materials to be protected are preferably natural, semisynthetic or preferably synthetic polymers. Particular preference is given to thermoplastic polymers, especially polyole-fins, in particular polyethylene and polypropylene or copolymers thereof with mono- and diolefins.

Particular emphasis is to be placed on the action of the novel compounds against thermal and oxidative degradation, especially under thermal stress as occurs during the processing of thermoplastics. The novel components (b), (c), (d) and (e) are therefore outstandingly suitable for use as processing (in-process) stabilizers.

The mixture of components (b), (c), (d) and (e) is also suitable for stabilizing polyolefins which are in long-term contact with extracting media.

Component (b) is preferably added to the organic material to be stabilized in an amount of from 0.0005 to 5%, in particular from 0.001 to 2%, for example from 0.01 to 2%, based on the weight of the organic material to be stabilized.

Components (c), (d) and (e) are judiciously added to the organic material to be stabilized in an amount of from 0.01 to 10%, for example from 0.01 to 5%, preferably from 0.025 to 3% and, in particular, from 0.025 to 1%, based on the weight of the organic material to be stabilized.

In addition to components (a), (b), (c), (d) and (e) the novel compositions may comprise further costabilizers (additives) the following, for example:

1. Antioxidants

- 1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-di-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol and mixtures thereof.
- 1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.
- 1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octade-cyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.
- 1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (Vitamin E).
- 1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)disulfide.
- 1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)-phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butyl-phenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylben-zyl)-4-nonylphenol], 2,2'-methylenebis[6-(α -methylenebis[6-(α -methylenebis(2,6-di-tert-butyl-2-methylphenol), 1,1-bis(5-lenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-

tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

- 1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.
- 1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-te-tramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.
- 1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.
- 1.10. Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxy-anilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxyben-zyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

- 1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.
- 1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.
- 1.13. Esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylol-propane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.
- 1.14. Esters of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.
- 1.15. Esters of β-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.
- 1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)ox-

amide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Naugard*XL-1 supplied by Uniroyal).

1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N.N'-bis(1butyl-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-Nf-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenlenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dime-4.4'-diaminodiphenylmethane. 2.4'-diaminodiphenylmethane, thylaminomethylphenol, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tertoctylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tertoctyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- und dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- und dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- und dialkylated tert-octyl-phe-N-allylphenothiazin, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N.N-bisnothiazines,

(2,2,6,6-tetramethyl-piperid-4-yl-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)-sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

- 2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-ditert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl- 2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α , α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2methoxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenylbenzotriazole, 2,2'-methylene-bis[4-(1,1,3,3tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol $[R-CH_2CH_2-COO-CH_2CH_2]_2$ where R=3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl, 2-[2'-hydroxy-3'- $(\alpha,\alpha$ -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)-phenyl]benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α , α -dimethylbenzyl)-phenyl]benzotriazole.
- 2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.
- 2.3. Esters of substituted and unsubstituted benzoic acids, as for example 4-tertbutyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzo-

ate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β , β -diphenylacrylate, isooctyl α -cyano- β , β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxy-cinnamate, butyl α -cyano- β -methyl-p-methoxy-cinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetrame-thylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate. bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyi)-2-n-butyl-2-(2-hydroxy-3,5-di-tertbutylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate. bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetrame-

3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolithyl-4-piperidyl)pyrrolidin-2,5-dione, dine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2.2.6.6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-do-N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimid, decylsuccinimid, 2-undecvi-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro [4,5]decane und epichlorohydrin, 1,1bis(1,2,2,6,6-pentamethyl-4-piperidyloxycarbonyl)-2-(4-methoxyphenyl)ethene, N.N'-bisformyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, diester of 4-methoxymethylene-malonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, reaction product of maleic acid anhydride-αolefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4aminopiperidine.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-diodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-2,4-bis(2-hydroxy-4-pro-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, pyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis-(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphe-2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-trinyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5azine. 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxy-phenyl]-4,6-bis(2,4-ditriazine. 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5bis(2.4-dimethylphenyl)-1,3,5-triazine, triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3butoxy-2-hydroxy-propoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-{2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl}-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

- 3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyladipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.
- 4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-ditert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecyloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butyl-phenyl)) pentaerythritol diphosphite, tristearyl sorbitoly triphosphite, tetrakis(2,4-di-tert-butyl-phenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz-[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, 2,2',2"-nitrilo[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite.
- <u>5. Hydroxylamines</u>, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dieth
- 6. Nitrones, for example, N-benzyl-alpha-phenyl-nitrone, N-ethyl-alpha-methyl-nitrone, N-octyl-alpha-heptyl-nitrone, N-lauryl-alpha-undecyl-nitrone, N-tetradecyl-alpha-tridcyl-nitrone, N-hexadecyl-alpha-pentadecyl-nitrone, N-octadecyl-alpha-heptadecyl-nitrone, N-hexadecyl-alpha-heptadecyl-nitrone, N-heptadecyl-alpha-hep-

tadecyl-nitrone, N-octadecyl-alpha-hexadecyl-nitrone, nitrone derived from N,N-dialkylhy-droxylamine derived from hydrogenated tallow amine.

- 7. Thiosynergists, for example, dilauryl thiodipropionate or distearyl thiodipropionate.
- 8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.
- 9. Polyamide stabilisers, for example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.
- 10. Basic co-stabilisers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zink pyrocatecholate.
- 11. Nucleating agents, for example, inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds such as ionic copolymers (ionomers).
- 12. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.
- 13. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

The costabilizers are added, for example, in concentrations of from 0.01 to 10%, based on the overall weight of the organic material to be stabilized.

The fillers and reinforcing agents (item 12 in the list), for example talc, calcium carbonate, mica or kaolin, are added to the polyolefin in concentrations, for example, of from 0.01 to 40%, based on the overall weight of the polyolefin to be stabilized.

The fillers and reinforcing agents (item 12 in the list), for example metal hydroxides, especially aluminium hydroxide or magnesium hydroxide, are added to the polyolefin in concentrations, for example, of from 0.01 to 60%, based on the overall weight of the polyolefin to be stabilized.

Carbon black as filler is added to the polyolefin in concentrations, judiciously, of from 0.01 to 5%, based on the overall weight of the polyolefin to be stabilized.

Glass fibers as reinforcing agents are added to the polyolefin in concentrations, judiciously, of from 0.01 to 20%, based on the overall weight of the polyolefin to be stabilized.

Further preferred compositions comprise in addition to components (a) to (e) further additives as well, especially alkaline earth metal salts of higher fatty acids, for example calcium stearate.

As a conventional stabilizer combination for processing polymeric organic materials, for example polyolefins, to form corresponding mouldings, the combination of a phenolic anti-oxidant with a secondary antioxidant based on an organic phosphite or phosphonite is recommended. Depending on the particular substrate and process, however, many polyolefin processors are forced to operate processes in the high-temperature range above about 280°C. By virtue of the incorporation of a novel processing stabilizer mixture of components (b), (c), (d) and (e), which is especially suitable for high-temperature applications, in particular in the temperature range above 300°C, industrial materials and mouldings, based for instance on high-density polyethylene, for example pipes and their technical variants (fittings), can be produced at a greater rate and with fewer rejects. Another advantage of this stabilizer mixture is that it can be employed in very small amounts. This leads to a reduction in the overall concentration of antioxidant relative to conventional stabilizer mixtures. Thus

the use of a low concentration of a stabilizer of the benzofuran-2-one type [component (b)] allows a reduction in the overall concentration of stabilizer by about a third in polyolefins, for example, which simultaneously represents an economic advantage.

The incorporation of components (b), (c), (d) and (e), and further additives if desired, into the polymeric, organic material is carried out by known methods, for example prior to or during shaping or else by applying the dissolved or dispersed stabilizer mixture to the polymeric organic material, with or without subsequent evaporation of the solvent. The stabilizer mixture of components (b), (c), (d) and (e) with or without further additives, can also be added in the form of a masterbatch, which contains these components in a concentration, for example, of from 2.5 to 25% by weight, to the materials that are to be stabilized.

The stabilizer mixture of components (b), (c), (d) and (e), with or without further additives, can also be added before or during polymerization or prior to crosslinking.

The stabilizer mixture of components (b), (c), (d) and (e), with or without further additives, can be incorporated in pure form or encapsulated in waxes, oils or polymers into the organic material that is to be stabilized.

The stabilizer mixture of components (b), (c), (d) and (e), with or without further additives, can also be sprayed onto the polymer that is to be stabilized. It is able to dilute other additives (for example the conventional additives indicated above) or their melts so that they too can be sprayed together with these additives onto the polymer that is to be stabilized. Addition by spraying on during the deactivation of the polymerization catalysts is particularly advantageous, it being possible to carry out spraying using, for example, the steam used for deactivation.

In the case of spherically polymerized polyolefins it may, for example, be advantageous to apply the stabilizer mixture of components (b), (c), (d) and (e), with or without other additives, by spraying.

The materials stabilized in this way can be employed in a wide variety of forms, for example as films, fibres, tapes, moulding compositions, profiles or as binders for coating materials, especially powder coatings, adhesives or putties.

The polyolefins stabilized in this way can likewise be employed in a wide variety of forms, especially as thick-layer polyolefin mouldings which are in long-term contact with extractive media,, for example pipes for liquids or gases, films, geomembranes, strips, profiles or tanks.

The preferred thick-layer polyolefin mouldings have a layer thickness of from 1 to 50 mm, in particular from 1 to 30 mm, for example from 2 to 10 mm.

As already mentioned, the organic materials to be protected are preferably organic, especially synthetic, polymers. In this context, thermoplastic materials are protected with particular advantage. Attention should be drawn above all in this context to the outstanding activity of the novel stabilizer mixture of components (b), (c), (d) and (e) as in-process stabilizers (heat stabilizers). For this purpose they are advantageously added to the polymer prior to or during its processing. However, other polymers too (for example elastomers) or lubricants or hydraulic fluids can be stabilized against degradation, for example light-induced or thermo-oxidative degradation. Elastomers can be taken from the above listing of possible organic materials.

The lubricants and hydraulic fluids in question are based, for example, on mineral oils or synthetic oils or on mixtures thereof. The lubricants are familiar to the skilled worker and are described in the relevant technical literature, for example in Dieter Klamann, "Schmierstoffe und verwandte Produkte" (Verlag Chemie, Weinheim, 1982), in Schewe-Kobek, "Das Schmiermittel-Taschenbuch" (Dr. Alfred Hüthig-Verlag, Heidelberg, 1974) and in "Ullmanns Enzyklopädie der technischen Chemie", Vol.13, pages 85-94 (Verlag Chemie, Weinheim, 1977).

A preferred embediment of the present invention is therefore the use of components (b), (c), (d) and (e) as stabilizers, especially in-process stabilizers (thermal stabilizers), for organic materials, especially thermoplastic polymers, against oxidative, thermal or light-induced degradation.

The present invention also relates to a stabilizer mixture comprising (i) at least one compound of the benzofuran-2-one type, (ii) at least one compound from the group of the orga-

nic phosphites or phosphonites, (iii) at least one compound from the group of the phenolic antioxidants, and (iv) at least one compound from the group of the sterically hindered amines.

Preference is also given to stabilizer mixtures in which the weight ratio of the components (i): (ii): (iii): (iv) is from 10:1:1:0.1 to 0.01:1:10:100, in particular from 5:1:1:0.1 to 0.01:1:1:10.

The novel stabilizer mixture of components (b), (c), (d) and (e) features excellent stability to hydrolysis and advantageous colour behaviour, i.e. little discoloration of the organic material during processing.

Organic materials which are stabilized with the components of the present invention are particularly well protected against light-induced degradation.

The present invention also relates to a process for stabilizing an organic material against oxidative, thermal or light-induced degradation, which comprises incorporating in or applying to said material at least one each of components (b), (c), (d) and (e).

Preference is given to a process for stabilizing polyolefins that are in long-term contact with extractive media, wherein the polyolefins are thick-layer polyolefin mouldings and have a layer thickness of from 1 to 50 mm, in particular from 1 to 30 mm, for example from 2 to 10 mm, which comprises incorporating in or applying to said polyolefins at least one each of components (b), (c), (d) and (e).

Also of particular interest is a process for stabilizing thick-layer polyolefin mouldings that are in long-term contact with extractive media, wherein the thick-layer polyolefin mouldings are pipes or geomembranes, which comprises incorporating in or applying to said mouldings at least one each of components (b), (c), (d) and (e).

The term geomembranes refers to films which are employed, for example, in landfill sites and are required to have a service life of up to 300 years.

Extractive media are, for example, liquid or gaseous inorganic or organic materials.

Examples of gaseous inorganic materials are oxygen; nitrogen; oxides of nitrogen; for example NO, laughing gas or NO₂; oxides of sulfur, for example sulfur dioxide; halogens, for example fluorine or chlorine; Brönstedt acids, for example hydrofluoric acid, hydrochloric acid, hydroiodic acid or hydrocyanic acid; or bases, for example ammonia.

Examples of gaseous organic materials are C₁-C₄alkanes, for example methane, ethane, propane or butane; carbon monoxide; carbon dioxide; or phosgene.

Examples of liquid inorganic materials are water, chlorinated drinking water or aqueous salt solutions, for example sodium chloride solution (brine) or sodium sulfate solution; bromine; acid halides, e.g. titanium tetrachloride, thionyl chloride, nitrosyl chloride or trimethylsilyl chloride; alkalis, for example aqueous sodium hydroxide (NaOH), aqueous potassium hydroxide (KOH), aqueous ammonia solution, aqueous sodium bicarbonate solution or aqueous sodium carbonate solution.

Examples of liquid organic materials are organic solvents or liquid organic reagents.

Examples of organic solvents are aliphatic hydrocarbons, for example pentane, hexane, heptane, octane, petroleum spirit, nonane or decane; alcohols, for example methanol, ethanol, isopropanol, butanol, pentanol, amyl alcohol, cyclohexanol, pentaerythritol, ethylene glycol, ethylene diglycol, methylcellosolve, polyethylene glycol or glycerol; ketones, for example acetone, diethyl ketone, methyl ethyl ketone, diphenyl ketone or cyclohexanone; ethers, for example diethyl ether, dibutyl ether, tetrahydrofuran or dioxane; aromatic hydrocarbons, for example benzene, toluene or xylene; heterocyclic solvents, for example furan, pyridine, 2,6-lutidine or thiophene; dipolar aprotic solvents, for example dimethylformamide, diethylacetamide or acetonitrile; or surfactants.

For the purposes of the present invention, extractive media are also mixtures and solutions, especially aqueous mixtures, emulsions or solutions, of liquid or gaseous inorganic and organic materials as listed above.

Of particular interest are those extractive media which are important in the chemical industry or in landfill sites.

A preferred embodiment of the present invention is therefore also the use of a stabilizer mixture of components (b), (c), (d) and (e), with or without further additives, for improving the stability of polyolefins that are in long-term contact with extractive media.

The preferred components (b), (c), (d) and (e) for the use as stabilizers, the process for stabilizing and the stabilizer mixture are the same as those described for the compositions with an organic material.

The examples which follow illustrate the invention in more detail. Parts and percentages are by weight.

Example 1: Stabilizing polyethylene that is in long-term contact with water.

0.1% by weight of calcium stearate and the stabilizers listed in Table 1 are added dry to a polyethylene polymer (Hostalen^e CRP 100; PE-HD) taken directly from the reactor, and the additives are incorporated in a Pappenmaier mixer (type 20) for two minutes (Examples 1a to 1c).

Table 1:

Examples	Stabilizers	Amount (% by wt.)
Example 1a ^{a)}	Irgafos [®] 168 ^{c)} Irganox [®] 1010 ^{d)} Chimassorb [®] 944 ^{e)}	0.10 0.10 0.20
Example 1b ^{b)}	Verbindung (101) ^{f)} Irgafos [®] 168 ^{c)} Irganox [®] 1010 ^{d)} Chimassorb [®] 944 ^{e)}	0.05 0.10 0.05 0.20
Example 1c ^{b)}	Verbindung (101) ^{f)} Irgafos [®] 168 ^{c)} Irganox [®] 1010 ^{d)} Chimassorb [®] 119 ^{g)}	0.05 0.10 0.05 0.20

a) Comparison example.

- b) Example according to the invention.
- c) Irgafos°168 (Ciba Spezialitätenchemie AG) is tris(2,4-di-tert-butylphenyl) phosphite.
- d) Irganox^e1010 (Ciba Spezialitätenchemie AG) is the pentaerythritol ester of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (compound of the formula VIc).
- e) Chimassorb 944 (Ciba Spezialitätenchemie AG) denotes linear or cyclic condensation products prepared from N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylendiamine and 4-tert-octylamino-2,6-dichlor-1,3,5-triazine [compound of the formula (H5)].
- f) Compound (101) is a mixture of about 85 parts by weight of the compound of the formula Va and about 15 parts by weight of the compound of the formula Vb.
- g) Chimassorb*119 (Ciba Spezialitätenchemie AG) denotes condensation products prepared from 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane [compound of the formula (H6)].

Irgafos[®]168, Irganox[®]1010, Chimassorb[®]944 and Chimassorb[®]119 are protected trade names of the company Ciba Spezialitätenchemie AG

In a Schwabenthan extruder the stabilized polyethylene is homogenized at 220°C and is processed at 300°C to granules. For the extraction experiments in water, test sheets measuring 44 mm by 20 mm by 2 mm are pressed from the granules of the individual formulations (Examples 1a to 1c) using a bench press. To facilitate the demoulding of the test sheets, pressing is carried out between two aluminium foils.

The stabilizer extraction experiments were carried out with deionized water. The thermal conditioning of the extraction containers takes place in a convection oven from Heraeus (Hanau, Germany) with a maximum temperature deviation of 1.5°C. For the extraction experiments below the boiling point of water, glass vessels are used. In the case of a water temperature of 105°C, stainless steel pressure vessels are employed. Owing to the risk of oversaturation of the water with stabilizer, the amount of liquid for the experiments is fixed at about 400 ml for about 70 g of polymer and the water is replaced at regular intervals of time, specifically after each sampling, by fresh water.

The test sheets are exposed at 80°C for 50 days to the experimental conditions described above. After the end of the extraction experiments, the residual stabilizer content and oxidation induction time (OIT) of the test sheets are measured.

The residual content of the sterically hindered phenol, Irganox $^{\circ}$ 1010, is determined with the aid of an internal standard in a HPLC instrument of the type Spectra Physics SP 8800 with autosampler and UV/VIS detector of the type Spectra 200. The chromatography is carried out at room temperature with a column of the hyperchrome type 125 x 4.6 mm, packed with Nucleosil C 185 μ m. The injection volume is 14 μ l at a flow rate of 1.5 ml/minute. UV detection takes place at 270 nm.

The residual content of the triazine-containing sterically hindered amines, Chimassorb® 944 and Chimassorb®119, is determined with a UV spectrometer of the Perkin Elmer Lambda 15 type by measuring the difference between the absorbances at 246.4 and 300 nm.

The oxidation induction time is determined by means of a "DuPont instrument 910 differential scanning calorimeter" from TA Instruments (Alzenau, Germany) and with a sample amount of from 5 to 10 mg, and describes the period of time, in minutes, under constant thermal stress (190°C/O₂) until complete decomposition of the polyethylene sample begins. The longer the oxidation induction time, the better the stabilization of polyethylene and the more stable the polyethylene with respect to extracted water which is in long-term contact with the polyethylene.

The results show that the stability of polyolefins that are in long-term contact with extracted media is improved if the stabilizer mixture comprises a novel component (b), (c), (d) and (e). The results are summarized in Table 2.

Table 2: Water storage for 50 days at 80°C

Example	Stabilizer	Residual stabilizer content after 50 days at 80°C	Oxidation induction time in minutes
1a ^{a)}	0,10% lrgafos [®] 168 ^{c)} 0,10% lrganox ³ 1010 ^{d)} 0,20% Chimassorb ³ 944 ^{e)}	52% 57%	34
1b ^{b)}	0,05% Compound (101) ^{f)} 0,10% Irgafos [®] 168 ^{c)} 0,05% Irganox [®] 1010 ^{d)} 0,20% Chimassorb [®] 944 ^{e)}	56% 71%	38
1c ^{b)}	0,05% Compound (101) ¹⁾ 0,10% Irgafos 168 ^{c)} 0,05% Irganox 1010 ^{d)} 0,20% Chimassorb 144 ^{d)}	57% 70%	39

Footnotes a) to g) see Table 1.

<u>Example 2</u>: Stabilizing polypropylene in the case of multiple extrusion and at especially high temperatures.

1.5 kg of polypropylene powder (Profax*6501), which has been initially stabilized with 0.008% of Irganox*1076 (compound of the formula VIb) (with a melt index of 3.2 measured at 230°C and under 2.16 kg), are mixed with 0.10% of calcium stearate and 0.015 to 0.20% of the stabilizers listed in Table 3. This mixture is extruded in an extruder having a barrel diameter of 20 mm and a length of 400 mm at 100 revolutions per minute, the maximum extruder temperature being set at 280, 300, 320 and 340°C. For cooling, the extrudate is drawn through a water bath and then granulated. These granules are extruded repeatedly. After 5 extrusions, the melt index is measured (at 230°C under 2.16 kg). A large increase in the melt index denotes severe chain breakdown and hence poor stabilization. The results are summarized in Table 3. They show that the stability of polypropylene is improved if the stabilizer mixture comprises a novel component (b), (c), (d) and (e).

Table 3:

Example	Stabilizers	Amount (% by wt.)	Melt index after 5 extrusions
Example 2a ^{a)}	Irgafos [®] 168 ^{c)} Irganox [®] 1010 ^{d)} Chimassorb [®] 944 ^{e)}	0.10 0.10 0.20	17.5
Example 2b ^{b)}	Compound (101) ^{f)} Irgafos [®] 168 ^{c)} Irganox [®] 1010 ^{d)} Chimassorb [®] 944 ^{e)}	0.015 0.10 0.05 0.10	8.6
Example 2c ^{b)}	Compound (101) ^{f)} Irgafos [®] 168 ^{c)} Irganox [®] 1010 ^{d)} Chimassorb [®] 119 ^{g)}	0.015 0.10 0.05 0.10	8.0

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Footnotes a) to g) see Table 1 of Example 1.

WHAT IS CLAIMED IS:

- 1. A composition comprising
 - a) an organic material which is subject to oxidative, thermal or light-induced degradation,
 - b) at least one compound of the benzofuran-2-one type,
 - c) at least one compound from the group of the organic phosphites or phosphonites,
 - d) at least one compound from the group of the phenolic antioxidants, and
 - e) at least one compound from the group of the sterically hindered amines.
- 2. A composition according to claim 1, comprising as component (b) a compound of the formula I

in which, if n is 1,

 R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, C_1 - C_4 alkylthio-, hydroxyl-, halo-, amino-, C_1 - C_4 alkylamino-, phenylamino- or di(C_1 - C_4 alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β -carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, or R_1 is a radical of the formula R_1

$$\begin{array}{c} R_9 \\ R_{7} \\ R_{8} \end{array} \qquad (II)$$

and

if n is 2,

 R_1 is unsubstituted or C_1 - C_4 alkyl- or hydroxyl-substituted phenylene or naphthylene; or is $-R_{12}$ -X- R_{13} -,

 R_2 , R_3 , R_4 and R_5 independently of one another are hydrogen, chlorine, hydroxyl, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl-amino, C_1 - C_2 5alkanoyloxy, C_1 - C_2 5alkanoyloxy, C_3 - C_2 5alkanoyloxy which

is interrupted by oxygen, sulfur or $N-R_{14}$; C_6-C_9 cycloalkylcarbonyloxy, benzoyloxy or

 C_1 - C_{12} alkyl-substituted benzoyloxy; or else the radicals R_2 and R_3 or the radicals R_3 and R_4 or the radicals R_4 and R_5 , together with the carbon atoms to which they are attached, form a benzo ring, R_4 is additionally -(CH_2)_p- COR_{15} or -(CH_2)_qOH or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of the formula III

$$R_{2}$$

$$R_{16}$$

$$C$$

$$R_{17}$$

$$(III)$$

in which R_1 is defined as indicated above for n=1, R_6 is hydrogen or a radical of the formula IV

$$R_2$$
 R_3
 R_4
 R_5
 R_5
 R_5

where R_4 is not a radical of the formula III and R_1 is defined as indicated above for n = 1, R₇, R₈, R₉, R₁₀ and R₁₁ independently of one another are hydrogen, halogen, hydroxyl, C_1 - C_{25} alkyl, C_2 - C_{25} alkyl interrupted by oxygen, sulfur or N- R_{14} ; C_1 - C_{25} alkoxy, C_2 - C_{25} alkoxy interrupted by oxygen, sulfur or $N-R_{14}$; C_1 - C_{25} alkylthio, C_3 - C_{25} alkenyl, C₃-C₂₅alkenyloxy, C₃-C₂₅alkynyl, C₃-C₂₅alkynyloxy, C₇-C₉phenylalkyl, C₇-C₉phenylalkoxy, unsubstituted or C1-C4alkyl-substituted phenyl; unsubstituted or C1-C4alkyl-substituted phenoxy; unsubstituted or C1-C4alkyl-substituted C5-C6cycloalkyl; unsubstituted or C1-C4alkyl-substituted C5-C8cycloalkoxy; C1-C4alkylamino, di(C1-C4alkyl)amino, C1-C25alkanoyl, C_3 - C_{25} alkanoyl interrupted by oxygen, sulfur or $N-R_{14}$; C_1 - C_{25} alkanoyloxy, C_3 - C_{25} alkanoyloxy interrupted by oxygen, sulfur or $N-R_{14}$; C_1-C_{25} alkanoylamino, C_3-C_{25} alkenoyl, C_3 - C_{25} alkenoyl interrupted by oxygen, sulfur or $N-R_{14}$; C_3 - C_{25} alkenoyloxy, C_3 - C_{25} alkenoyloxy interrupted by oxygen, sulfur or N-R₁₄; C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C1-C12alkyl-substituted benzoyl; benzoyloxy or C1-C12alkyl-substituted benzoyloxy; $-O-\stackrel{R_{18}}{\overset{}{\overset{}{\text{C}}}} \stackrel{O}{\overset{}{\overset{}{\text{C}}}} \stackrel{R_{20}}{\overset{}{\overset{}{\text{C}}}} \stackrel{R_{21}}{\overset{}{\overset{}{\text{C}}}}$ stituted benzoyloxy; $-O-\stackrel{C}{\overset{}{\overset{}{\text{C}}}} \stackrel{C}{\overset{}{\text{C}}} \stackrel{C}{\overset{}{\text{C}}} \stackrel{C}{\overset{}{\text{C}}} \stackrel{C}{\overset{}{\text{C}}} \stackrel{R_{21}}{\overset{}{\text{C}}}$, or else, in formular transfer of $\stackrel{C}{\overset{}{\text{C}}} \stackrel{C}{\overset{}{\text{C}}} \stackrel{C}{\overset{C}} \stackrel{C}} \stackrel{C}{\overset{C}} \stackrel{C} \overset{C} \overset{C} \overset{C}} \stackrel{C} \stackrel{C} \overset{C}} \stackrel{C} \stackrel{C} \overset{C} \overset{C}} \stackrel{C} \overset{C} \overset{C} \overset{C} \overset{C} \overset{C} \overset{C} \overset{C}} \stackrel{C} \overset{C}} \stackrel{C} \overset{C} \overset{C} \overset{C} \overset{C}} \stackrel{C} \overset{C} \overset{C}} \stackrel{C} \overset{C} \overset{C}} \stackrel{C} \overset{C} \overset{C} \overset{C} \overset{C}} \stackrel{C} \overset{C} \overset{C} \overset{C} \overset{C} \overset{C} \overset{C}} \stackrel{C} \overset{C}$

la II, the radicals R_7 and R_8 or the radicals R_8 and R_{11} , together with the carbon atoms to which they are attached, form a benzo ring,

R₁₂ and R₁₃ independently of one another are unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene,

R₁₄ is hydrogen or C₁-C₈alkyl,

$$R_{15}$$
 is hydroxyl, $\left[-0^{-\frac{1}{r}}M^{r+}\right]$, C_1 - C_{18} alkoxy or $-N$
 R_{25}

R₁₆ and R₁₇ independently of one another are hydrogen, CF₃, C₁-C₁₂alkyl or phenyl, or R₁₆ and R₁₇, together with the C atom to which they are attached, form a C₅-C₈cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

R₁₈ and R₁₉ independently of one another are hydrogen, C₁-C₄alkyl or phenyl,

R₂₀ is hydrogen or C₁-C₄alkyl,

R₂₁ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl, C₂-C₂₅alkyl

interrupted by oxygen, sulfur or $N-R_{14}$; C_7-C_9 phenylalkyl which is unsubstituted or

substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl; C₇-C₂₅phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl and

interrupted by oxygen, sulfur or $N-R_{14}$, or else the radicals R_{20} and R_{21} , together with

the carbon atoms to which they are attached, form a C_5 - C_{12} cycloalkylene ring which is unsubstituted or substituted from 1 to 3 times by C_1 - C_4 alkyl;

R₂₂ is hydrogen or C₁-C₄alkyl,

R₂₃ is hydrogen, C₁-C₂₅alkanoyl, C₃-C₂₅alkanoyl, C₃-C₂₅alkanoyl interrupted by oxygen, sulfur

or $N-R_{14}$; C_2-C_{25} alkanoyl substituted by a di(C_1-C_6 alkyl)phosphonate group;

C₆-C₉cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C₁-C₁₂alkyl-substituted benzoyl;

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R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₈alkyl,

R₂₆ is hydrogen or C₁-C₈alkyl,

R₂₇ is a direct bond, C₁-C₁₈alkylene, C₂-C₁₈alkylene interrupted by oxygen, sulfur or

N-R₁₄; C₂-C₁₈alkenylene, C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene,

C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene, unsubstituted or C₁-C₄alkyl-substituted phenylene,

$$\int_{0}^{\infty}$$
 or \int_{s}^{∞} .

$$R_{28}$$
 is hydroxyl, $\left[-0^{-\frac{1}{r}M}^{r+}\right]$, C_1 - C_{18} alkoxy or $-N$

$$R_{29}$$
 is oxygen, -NH- or $N-C-NH-R_{30}$,

R₃₀ is C₁-C₁₈alkyl or phenyl,

R₃₁ is hydrogen or C₁-C₁₈alkyl,

M is an r-valent metal cation,

X is a direct bond, oxygen, sulfur or -NR₃₁-,

n is 1 or 2,

p is 0, 1 or 2,

q is 1, 2, 3, 4, 5 or 6,

r is 1, 2 or 3, and

s is 0, 1 or 2.

3. A composition according to claim 1, comprising as component (b) a compound of the formula V

R₂ is hydrogen or C₁-C₆alkyl,

R₃ is hydrogen,

R₄ is hydrogen or C₁-C₆alkyl,

R₅ is hydrogen,

 R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy, with the proviso that at least two of the radicals R_7 , R_8 , R_9 , R_{10} or R_{11} are hydrogen.

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4. A composition according to claim 1, in which component (b) is a compound of the formula Va or Vb

or a mixture of the two compounds of the formula Va and Vb.

5. A composition according to claim 1, comprising as component (c) a compound of the formula 1, 2, 5 or 6

(1)
$$R'_1 - Y' - P'_{O-R'_3}$$
 $A' - \begin{bmatrix} O - R'_2 \\ O - R'_3 \end{bmatrix}_{n'}$ (2)

$$R'_{1}-O-P'_{0}-O-R'_{1}$$
 (5)

$$E' - P - Z' - R'_{14} - R'_{15} - R'_{14} - R'_{15} - R'_{14} -$$

n' is the number 2 and y' is the number 1, 2 or 3;

A' is C₂-C₁₈alkylene, p-phenylene or p-biphenylene,

E', if y' is 1, is C₁-C₁₈alkyl, -OR', or fluorine;

E', if y' is 2, is p-biphenylene,

E', if y' is 3, is $N(CH_2CH_2O_{-})_3$,

 R'_{1} , R'_{2} and R'_{3} independently of one another are C_{1} - C_{18} alkyl, C_{7} - C_{9} phenylalkyi, cyclohexyl. phenyl, or phenyl substituted by 1 to 3 alkyl radicals having in total 1 to 18 carbon atoms; R'_{14} is hydrogen or C_{1} - C_{9} alkyl,

R'15 is hydrogen or methyl;

X' is a direct bond,

Y' is oxygen,

Z' is a direct bond or -CH(R'16)-, and

R'16 is C1-C4alkyl.

- 6. A composition according to claim 1, in which component (c) is tris(2,4-di-tert-butylphenyl) phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite or tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite.
- 7. A composition according to claim 1, comprising as component (d) a compound of the formula VI

$$\begin{bmatrix}
H_3C \\
H_3C
\end{bmatrix}$$

$$X \longrightarrow H_2$$

$$R_1$$
(VI)

R₁ is C₁-C₄alkyl,

n is 1, 2, 3 or 4,

if n is 1.

X is
$$-CH_2-CH_2-C-Y-$$
, where Y is attached to R_2 , and R_2 is C_1-C_{25} alkyl; and,

if n is 2,

 R_2 is C_2 - C_{12} alkylene, C_4 - C_{12} alkylene interrupted by oxygen or sulfur; or, if Y is -NH-, R_2 is additionally a direct bond; and,

if n is 3,

X is methylene or $-CH_2-C-O-CH_2-CH_2-$, where the ethylene group is attached to R_2 , and

$$R_2$$
 is N N ; and

if n is 4,

X is —CH2—CH2—C—Y— , where Y is attached to R2, and

R₂ is C₄-C₁₀alkanetetrayl.

- 8. Composition according to claim 7, in which in the compound of the formula VI, if n is 1, R_2 is C_1 - C_{20} alkyl.
- 9. A composition according to claim 7, in which in the compound of the formula VI,

if n is 2,

 R_2 is C_2 - C_8 alkylene, C_4 - C_8 alkylene interrupted by oxygen or sulfur; or, if Y is -NH-, R_2 is additionally a direct bond; and,

if n is 4,

R₂ is C₄-C₈alkanetetrayl.

10. A composition according to claim 7, in which in the compound of the formula VI R₁ is methyl or tert-butyl, n is 1, 2 or 4,

Y is oxygen or -NH-; and,

if n is 1,

R₂ is C₁₄-C₁₈alkyl; and,

if n is 2,

 R_2 is C_4 - C_6 alkylene, or is C_4 - C_6 alkylene interrupted by oxygen; and,

if n is 4,

R₂ is C₄-C₆alkanetetrayl.

11. A composition according to claim 1, in which component (d) is at least one compound of the formula VIa, VIb, VIc or VId

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$$H_{3}C$$
 C
 CH_{3}
 CH_{2}
 CH_{2}
 CH_{2}
 CH_{2}
 CH_{3}
 CH_{3}

$$\begin{bmatrix}
H_{3}C \\
H_{3}C
\end{bmatrix}
CH_{2}
CH_{2}
CH_{2}
-CH_{2}
-C$$

12. A composition according to claim 1, in which component (e) comprises at least one radical of the formula XII or XIII

(XII)
$$G-CH_{2} \xrightarrow{CH_{3} G_{1}} G_{2}$$

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G is hydrogen or methyl, and

 G_1 and G_2 are hydrogen, methyl or together are oxygen.

13. A composition according to claim 1, in which component (e) is a compound of the formula H1, H2, H3, H4, H5, H6 or H7

$$H_{3}C$$
 CH_{3}
 CH_{3}

$$(CH_3)_3C$$

$$HO$$

$$CH_2$$

$$CH_2$$

$$CH_3$$

$$H_3C$$
 CH_3
 CH_3

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$$R' = H_{3}C - N - N - N - CH_{3}$$

$$H_{3}C - N - N - C_{4}H_{9} - N - C_{4}H_{9} - CH_{3}$$

$$CH_{3} -$$

m is a number from the range from 2 to 200.

- 14. A composition according to claim 1, comprising as component (a) a natural, semisynthetic or synthetic polymer.
- 15. A composition according to claim 1, comprising as component (a) a thermoplastic polymer.
- 16. A composition according to claim 1, comprising as component (a) a polyolefin.
- 17. A composition according to claim 1, comprising as component (a) polyethylene or polypropylene or a copolymer thereof with mono- and diolefins.
- **18.** A composition according to claim 1, comprising as component (a) a thick-layer polyolefin moulding.
- 19. A composition according to claim 18, in which the thick-layer polyolefin moulding has a layer thickness of from 1 to 50 mm.

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- 20. A composition according to claim 18, in which the thick-layer polyolefin moulding comprises polyolefin pipes or polyolefin geomembranes.
- 21. A composition according to claim 1, comprising as component (a) a polyolefin which is in long-term contact with extractive media.
- 22. A composition according to claim 21, in which the extractive medium is a liquid or gaseous inorganic or organic material.
- 23. A composition according to claim 1, in which component (b) is present in an amount of from 0.0005 to 5% based on the weight of component (a).
- 24. A composition according to claim 1, in which components (c), (d) and (e) are present in an amount of from 0.01 to 10% based on the weight of component (a).
- 25. A composition according to claim 1, comprising in addition to components (a), (b), (c), (d) and (e) further additives as well.

- 26. A stabilizer mixture comprising
 - i) at least one compound of the benzofuran-2-one type,
 - ii) at least one compound from the group of the organic phosphites or phosphonites,
 - iii) at least one compound from the group of the phenolic antioxidants, and
 - iv) at least one compound from the group of the sterically hindered amines.
- 27. A stabilizer mixture according to claim 26, in which the weight ratio of the components (i): (ii): (iii): (iv) is from 10:1:1:0.1 to 0.01:1:10:
- 28. A process for stabilizing an organic material against oxidative, thermal or light-induced degradation, which comprises incorporating in or applying to said material at least one each of components (b), (c), (d) and (e) according to claim 1.
- 29. The use of a mixture of components (b), (c), (d) and (e) according to claim 1 as stabilizers for organic materials against oxidative, thermal or light-induced degradation.





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GB 9802277.5

1 to 29

Examiner:

Miss M. M. Kelman

Date of search:

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Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C3K KCZ, C3M MA

Int Cl (Ed.6): C08K 5/00, 5/15, 5/3435

Other: ONLINE: CHABS, CLAIMS, JAPIO, RAPRA, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		
X,P	GB 2315070 A	CIBA SPECIALTY CHEMICALS see the claims, page 64, lines 11 to 19, page 65, lines 11 to 18, page 74, lines 21 to 22, and Examples 1,2,4 and 5	1 to 17,21,22,2 3,24,25,26 ,28,29
A,P	GB 2311528 A	CIBA SPECIALTY CHEMICALS	
Α	GB 2293827 A	SANDOZ	
Α	US 5516920 A	CIBA-GEIGY	

& Member of the same patent family

- A Document indicating technological background and/or state of the art.

 P Document published on or after the declared priority date but before
- P Document published on or after the declared priority date but before the filing date of this invention.
- E Patent document published on or after, but with priority date earlier than, the filing date of this application.

X Document indicating lack of novelty or inventive step

Y Document indicating lack of inventive step if combined with one or more other documents of same category.